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"DEFECT STATES IN PLASMA-DEPOSITED
a-Si:H"

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Overview

This report comprises four preprints that describe the contract work performed and completed during the report period. A summary of the results follows.

1) Glow Discharge Optical Spectroscopy (GDOS).

This experiment measures the total concentration of an added impurity (in this case boron), by analysing the spectral emission lines of an argon plasma during sputtering of the sample. A substantially larger ratio of boron to silicon is found in the film compared to that in the deposition gas. This enhancement is dependent on the plasma operating conditions during sample preparation. The boron concentration measured by GDOS is calibrated using SIMS.

2) Growth and Microstructure of a-Si:H.

The nucleation and growth process of a-Si:H films is shown to be sensitive to the plasma operating conditions, and directly influences the electronic properties of the films. In films of a high defect density, growth is generally microscopically inhomogeneous and has a columnar morphology. The columns can be observed in SEM and by neutron and small angle x-ray scattering. Low defect density material shows no columnar structure within the available resolution. There is also evidence that the growth process is affected by substrate type.

3) Defect and Electronic States.

We show that light induced ESR and luminescence experiments observe the same excited electronic states. The experiments identify the ESR resonances of defect states and band tail electrons and holes. From measurements on samples of differing doping, it is shown that the defect ESR arises from dangling bonds with a positive electronic correlation energy.

4) Oxygenated a-Si:H.

Films prepared from $\text{SiH}_4/\text{O}_2/\text{Ar}$ gas mixtures have been prepared. The oxygen content of the film is much larger than that of the deposition gas. The oxygen is predominately incorporated as Si-O-Si units. With the addition of oxygen, the band gap increases, both the luminescence peak position and line-width increase, and thermal quenching of luminescence occurs at a higher temperature. The results indicate an increase in the band tail widths, and in the strength of the electron-phonon interaction.

**GLOW DISCHARGE OPTICAL SPECTROSCOPY MEASUREMENT OF DOPANT
CONCENTRATIONS IN a-Si:H***

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We report the results of glow discharge optical spectroscopy (GDOS) measurements of total dopant concentrations in a-Si:H films. Significant differences (up to a factor of 4.8) were found between the ratio of boron to silicon of the films and that of their deposition plasmas.

INTRODUCTION

There are two principle motivations for implementing a technique for the quantitative determination of dopant concentrations in a-Si:H films. One arises from the need to fully characterize the effects of varying deposition conditions while the other springs from the need for interlaboratory reproducibility. Optimization of the electronic properties of doped a-Si:H films requires the growth of films under various conditions of deposition. Since these changes in growth parameters may effect both the efficiency of dopant incorporation into the growing film as well as the dopant's subsequent electrical activity, direct measurement of dopant levels in the films themselves is required. Secondly, the literature of plasma deposited a-Si:H has heretofor simply cited the dopant-to-silicon ratio in the growth plasma to characterize dopant concentrations in grown films.¹ But because the mechanisms of dopant incorporation are incompletely understood, identical dopant ratios in the plasma may not be sufficient to guarantee identical concentrations in films grown in different laboratories, again indicating the need for direct measurements.

RF glow discharge optical spectroscopy (GDOS) was chosen as the technique for such analyses because it is characterized by the following: (1) Absolute values of dopant concentrations can be found; (2) it is insensitive to the form or orientation of the sample matrix, be it amorphous, poly- or single-crystalline; (3) sensitivity to low dopant concentrations is obtained with relatively inexpensive apparatus; (4) either electrically insulating or conducting films may be examined; and (5) analysis can be performed on samples in film form, as grown. This technique is the RF sputtering analog to DC GDOS, developed and used as a versatile tool for elemental analysis in bulk and thin film samples by Greene and co-workers.²⁻⁵ In this paper we present a

description of the GDOS apparatus, measurement conditions, calibration procedures, and the results of dopant concentration measurements of various a-Si:H samples.

EXPERIMENTAL PROCEDURES

GDOS analysis is accomplished by RF sputter-etching the sample of interest in an inert-gas plasma (argon, in this case). The sample's constituent atoms, ejected from the sample surface primarily as neutrals,⁶ are subsequently excited in the plasma and, upon decay, emit radiation of a characteristic wavelength. The intensities of two selected emission lines are measured, one from the dopant species, the other from the matrix. The ratio of these intensities, $I_{\text{dopant}}/I_{\text{matrix}}$, is a relative measure of the sample's dopant concentration. The results are made quantitative by analyzing standards of known dopant concentration.

The GDOS system is shown schematically in Fig. 1. The sample chamber is a diode sputtering system, the cathode of which is supplied with 13.54 MHz RF power

Fig. 1 Schematic diagram of RF GDOS system.

through a π matching network. Two slightly different sample assemblies can be mounted to the water-cooled cathode. One, used for the dopant concentration standards, consists of a silicon wafer bonded directly to a copper disc. The other consists of a disc of spectroscopic grade graphite similarly bonded to a copper substrate. The a-Si:H film is deposited on the graphite after the components of the sample assembly are joined. All samples are 3.3 cm in diameter. Sputter-etching is confined to the top of the sample assembly by means of an aluminum sheath, part of the anode, conformal with the sides of the cathode and closer to it than the length of the dark space. The body of the vacuum chamber is stainless steel with a fused silica window 23 cm from the sample's center. There is virtually no deposition on this window due to its distance from the plasma and the fact that it is upstream from the argon inlet. All optical components in the system are ultraviolet transmitting fused silica. Pressure in the sample chamber is monitored manometrically

During a measurement, light from the plasma traverses the chamber window and a collecting lens and is then divided by a beamsplitter. A small fraction goes through a narrow-pass filter centered on the strong neutral silicon line at 2516.1Å and into a photomultiplier. This signal is used to monitor the variations in the sample sputtering rate throughout the run. These variations are typically less than 5%. The bulk of the signal passes into a 0.6 meter, double-pass scanning monochromator. The system has a spectral resolution of 0.17Å, thus avoiding problems with overlapping emission peaks for the elements of interest. The photomultiplier at the monochromator's output connects to standard photon-counting equipment, then to a chart recorder. The information collected during a measurement consists of the intensity of two

selected emission lines, one from the dopant and one from the matrix species (from the monochromator) and the instantaneous etch rate at the times of those readings (from the silicon line monitor). The intensities of the sample and matrix emission lines are normalized to a common etch rate and $I_{\text{dopant}}/I_{\text{matrix}}$ calculated.

Standardized measurement conditions were used in all runs. Following purging and evacuation, a flow of high purity argon at 85 mTorr was established through the chamber. Pressure variations during a run (7-25 min) were $\leq 5\%$. 100 watts RF power raised the DC peak cathode voltage to -2000V. Equilibrium sputtering conditions were typically obtained within 90 seconds after ignition of the plasma.

CALIBRATION

In order for GDOS to quantitatively determine unknown boron concentrations in silicon matrices, a system calibration curve is needed relating GDOS measured $I_{\text{Boron}}/I_{\text{Silicon}}$ ratios to absolute boron dopant levels. To this end, six sets of boron doped silicon wafers of various resistivities were obtained. Initially it was planned to use the measured resistivities of these calibration wafers to determine their absolute boron concentrations and thus calibrate the GDOS $I_{\text{Boron}}/I_{\text{Silicon}}$ ratios. However, because there are three conflicting analytic expressions in the literature for this resistivity to dopant concentration conversion, an unambiguous calibration of GDOS could not be obtained by this method.⁷⁻⁹ It was therefore decided to cross-calibrate the GDOS measurements with a SIMS determination of the absolute boron concentration in the calibration wafers.

Using a Cameca IMS-3F ion microprobe, a SIMS measurement of the ratio of ^{11}B to ^{30}Si of one wafer from each of the six sets was made. During the same measurement the peak $^{11}\text{B}/^{30}\text{Si}$ ion intensity ratio of a 30 KeV, ^{11}B implanted Si wafer was determined. By use of dose and range statistics the peak boron concentration of this implant was known to be $5.39 \times 10^{20} \text{ B/cm}^3 \pm 20\%$.¹⁰ This data was used to quantify the concentration of boron in the six calibration wafers. GDOS had previously been

Fig. 2 GDOS vs SIMS determination of relative boron concentration in crystalline silicon wafers.

used to measure the relative intensities of the B 2497.7Å and Si 2516.1Å emission lines from a second wafer from each set. A small correction (0.7%) was applied to each GDOS data point to account for intraset variation in boron concentration. The size of this correction was determined from four-point probe resistivity measurements which, though not an acceptable means to quantify absolute dopant concentrations, were quite adequate for finding small relative differences. The resultant GDOS calibration curve is seen in Fig. 2. A linear plot of the same GDOS vs. SIMS data shows that no point deviates from linearity by more than 6%. The detectability limit for boron in silicon was found to be 1×10^{17} atoms/cm³ with the GDOS system as presently configured. Arsenic and phosphorous doped Si wafers were also examined under identical measurement conditions. The emission lines used were As 2288.1Å and P 2136.2Å. The detectability limit for both of these dopants was determined to be 3×10^{18} atoms/cm³.

RESULTS AND DISCUSSION

Three growth parameters of RF plasma-deposited a-Si:H films were varied and the dopant concentrations of the resultant films analyzed using GDOS. The growth apparatus and procedures have previously been described.¹¹ Films were grown with three different ratios of boron to silicon in the growth plasma; 2×10^{-5} , 2×10^{-4} and 2×10^{-3} . Anode films were grown upon substrates at 30°C and 230°C and, finally, films were grown with 20-22 watts, 5% reactive gas and 1 watt, 100% reactive gas. Both anode (unbiased) and cathode (biased) samples were examined under each set of growth conditions and the results plotted in Fig. 3.

Fig. 3 Boron concentration in a-Si:H films vs ratio of B to Si atoms in growth plasma. A point representing a film whose ratio of B to Si atoms was the same as that of its growth plasma would fall upon the solid line.

The most obvious feature of Fig. 3 is that all the films examined have boron to silicon ratios significantly (2.5 to 4.8 times) higher than that of their deposition plasma. Second, for anode samples, dopant incorporation efficiency is 50% higher for 1 watt, 100% films than for 20 watt, 5% films. Third, anode samples grown on heated substrates incorporate 20% less boron than do their ambient substrate analogues. Over the explored range of deposition parameters, used to grow very high to very low defect concentration a-Si:H films, dopant incorporation efficiency varies by nearly a

factor of two. Reliance on the B to Si ratio in the growth plasma as a measure of the dopant concentration in a-Si:H films may thus introduce errors of nearly 100% in studies of the electrical activity of incorporated boron atoms as a function of film growth parameters.

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GROWTH MORPHOLOGY AND DEFECTS IN PLASMA-DEPOSITED a-Si:H FILMS*

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Structural studies of plasma-deposited a-Si:H are presented that show that a major class of defect is an anisotropic density fluctuation. Studies of the hydrogen environment suggest that an inhomogeneous hydrogen distribution is associated with these fluctuations. From considerations of the deposition chemistry and nucleation theory a model is proposed to describe the film growth process and its relationship to defects.

INTRODUCTION

To the extent that a low density of defects is the primary feature that distinguishes plasma-deposited amorphous silicon from other forms of amorphous silicon, it is surprising that very little is known about the nature of these defects. In addition, although it is well known that hydrogen is present in the material and that its removal leaves behind a high density of defects, it has not been determined whether hydrogen is solely responsible for the low defect density or whether the material has an intrinsically less defective structure.

It is the purpose of this paper to discuss the results of a number of studies that address both this latter question and that of the nature of the defects. From a combination of structural measurements it is concluded that the primary type of defect is a density fluctuation created by the imperfect coalescence of nuclei formed in the initial stages of growth. It is shown that the location of the nucleation sites is influenced by the substrate material and that the rate-limiting reaction in film growth occurs at the surface, is reversible, and is probably itself dependent on substrate material. The effects of this process on hydrogen environments, internal stress in the film and subsequent chemical stability are described. In particular it is proposed from a combination of NMR, IR, and hydrogen evolution data that the hydrogen distribution can develop inhomogeneities associated with those observed structurally. Comparisons are made between these results, those of Barna and co-workers¹ on two dimensional nucleation and those of Lampe and co-workers^{2,3} on the photochemistry of silane. From these comparisons it is proposed that the plasma-deposition process produces an inherently less-defective structure due to a higher surface mobility for silicon hydride ($\text{SiH}_2, \text{SiH}_3$) species on growing nuclei.

SAMPLE PREPARATION

An R.F. diode deposition system was used,⁴ the variable parameters being substrate

temperature, R.F. power (0-30 watts), surface electrical bias (0 to -200 volts) and silane concentration (1-100% in argon). Other parameters were kept fixed. A previous study⁴ of luminescence and E.S.R. has identified the following correlations between these parameters and the density of defects that act as non-radiative recombination centers. Increasing the substrate temperature under all sets of parameters results in a reduction of defect center density until a minimum is reached in the range 230-300°C. At 230°C a minimum defect density is found with pure silane and low R.F. power. Dilution with argon and/or increase of R.F. power leads to higher defect densities except when the substrate surface is self-biased to some negative D.C. potential.

Systematic trends in hydrogen content and bonding configurations exist over the same parameter space.⁵ These can be summarized as follows. Material deposited at room temperature has the majority of its hydrogen (25-40 at%) bound as dihydride units (SiH_2) which, on unbiased substrates, are linked into $(\text{SiH}_2)_n$ chains. On raising the substrate temperature to 230-350°C the hydrogen content decreases to < 8 at% in material with the lowest defect density (pure SiH_4 , low R.F. power) and the bonding configuration becomes predominantly monohydride. If R.F. power or argon dilution are increased, dihydride units become increasingly favored, again linked to form $(\text{SiH}_2)_n$ on unbiased surfaces.

EXPERIMENT

Structure

Previous transmission electron microscopy of plasma-deposited a-Si:H by Barna et al.⁶ indicated that material, presumably prepared under optimum (low power, pure SiH_4) conditions, showed no visible microstructure. This finding is confirmed by the current study,⁷ and is illustrated in Fig. 1(c) for a 100%:1watt:230°C sample. The corresponding scanning electron micrograph of a fracture surface of a thick ($\sim 10\mu$) film is shown in Fig. 1(a). It is featureless and elsewhere shows evidence of

Fig. 1 (a) and (b) Scanning electron micrographs of fracture surfaces (perpendicular to substrate) of a-Si:H films: (a) 100%, 1W, 230°C; (b) 5%, 25W, 25°C; (c) and (d) Transmission electron micrographs of a-Si:H films deposited onto carbon-coated grids; (c) 100%, 1W, 230°C; (d) 5%, 25W, 25°C.

conchoidal fracture characteristic of amorphous or vitreous materials. In contrast, a sample prepared under conditions known to produce large defect densities, 5%:25watts:25°C, has the structure depicted in Figs. 1(d) and 1(b).

Viewed from the perspective of previous work on thin film growth the obvious interpretation of the island structure shown in 1(d) is that the film nucleates and grows from a finite number of nuclei into islands that fail for some reason to coalesce. The fact that the film is continuous and can be removed whole from a substrate suggests that the electron density fluctuations are at least partly representative of inhomogeneity rather than voids--this issue will be addressed later. What is of interest is that within the range of thickness accessible by TEM, the island dimensions do not change substantially suggesting columnar or rod-like growth with diameters $\sim 100\text{\AA}$. This suggestion has been confirmed directly by Leadbetter et al.⁸ using small angle X-ray and neutron scattering. Strongly anisotropic small angle scattering is found in all samples that show the columnar fracture surfaces and island structure. This is illustrated in Figs. 2(a) and (b) which show isotropic scattering contours with the neutron beam normal to the sample surface but anisotropic scattering when the sample is tilted at 60° . Analysis of the small angle scattering

FIGURE 2
Neutron scattering intensity contours for a 3%:25W:25°C sample (a) $\theta = 0^\circ$ (b) $\theta = 60^\circ$.

data indicates that, over the range of deposition space parameter so far examined, the magnitude of the scattering varies substantially, being undetectable in a 100%:2watt:230°C sample (similar to Fig. 1(a) and (c)), but the characteristic column diameter extracted from the analysis remains very nearly constant at $\sim 65\text{\AA}$. Since this data is taken from samples $\sim 50\mu$ thick, it follows that the islands seen in TEM do indeed propagate as columns with similar lateral dimensions.

Of particular interest is the manner in which the transition from a visible island structure to the featureless structure observed in Fig. 1(c) is accomplished. This transition is illustrated in Figs. 3(a), (b), and (c) which show the effect of reducing R.F. power on an unbiased substrate, with the substrate temperature and silane concentration kept constant at 230°C and 5%. The major change is a decrease in the resolution or area fraction of the interstitial regions. The island dimensions are, to first approximation, unchanged. Figs. 3(d), 3(c) and 1(c) form a similar series where only the concentration of silane is varied. The conclusion drawn from these figures is that the major effect of changing deposition parameters other than temperature and bias is to affect the coalescence of the islands.

FIGURE 3

Transmission electron micrographs of a-Si:H films deposited onto carbon-coated grids at $T_s = 230^\circ\text{C}$; (a) 5%, 25W; (b) 5%, 10W; (c) 5%, 1W; (d) 1%, 1W.

FIGURE 4

(a) electron spin density; (b) ratio of peak absorption constants of 845 cm^{-1} $(\text{SiH}_2)_n$ to 2100 cm^{-1} $(\text{SiH}_2 + (\text{SiH}_2)_n)$ Si-H vibrational modes for 5%:230°C samples as a function of R.F. power.

The effects of bias (sample placed on hot R.F. electrode) and substrate temperature are more complex. At 230°C the effect of bias on TEM and SEM is to remove all traces of island structure or columnar morphology. The correlation of this effect with the behavior of defect states is remarkably good. Figure 4(a) illustrates the variations in electron spin density with R.F. power with and without bias under the same conditions as Fig. 3 (5%, 230°C). For low T_s (25°C), the behavior is more complex. For example a sample deposited with low bias (~ 20 volts) and low power from pure SiH_4 at 25°C shows strong *isotropic* small angle scattering indicating another class of density fluctuation.

Substrate-Dependent Effects

In the course of the structural studies summarized above, TEM samples were prepared on a range of substrate materials and subsequently removed for examination by etching away the substrates. On two types of substrate striking effects were observed that appear to be related to preferential nucleation on surface structures in the substrate. Figures 5(a) and (b) show the effects observed on aluminum foil and a carbon film. Surface structures, presumably boundaries of aluminum grains elongated in the foil rolling process, act as either nucleation sites or barriers to island growth producing the observed *linear* island arrays. A similar phenomenon appears to occur in Fig. 5(b) although the origin of the structure is unclear. It is worth commenting that Freeman et al.⁹ observed structures in a-Si deposited on NaCl crystals by the Dundee group although the published micrographs do not permit direct comparison with our results.

Given that the morphology of a film can be influenced by the nature of the substrate via the nucleation process, it is relevant to a number of potential applications of a-

FIGURE 5

Transmission electron micrographs of a-Si:H films deposited onto (a) aluminium foil (b) carbon support film.

Si:H to ask whether electronic properties are also influenced by the substrate material. Recent work in our laboratory suggests that they are, at least in certain cases. Figure 6 shows luminescence emission spectra taken from two areas of an a-Si:H film deposited under low defect level conditions. The film is several microns thick while the laser light is absorbed in the top 1000Å. The substrate is fused silica over part of which a sputtered nickel film has been deposited. there is clearly a large reduction in the luminescence intensity over the nickel compared to the glass. The origin of this effect is uncertain. Interference effects can be ruled out since the fringe spacing seen in both spectra is less than the emission line width. Two possibilities are higher defect densities or different surface topologies leading to different light scattering at the surface. Independent of the detailed explanation these results suggest that substrate-dependent changes in electronic properties should be considered when comparing data on different sample configurations.

FIGURE 6

Luminescence emission spectra (10°K) for a 100%:1W:230°C sample deposited onto partly nickel coated fused silica substrate.

Finally, it is found that gross surface features or debris on the surface can act as nucleation centers for a much larger type of defect. This defect is illustrated in Figs. 7(a) and (b) which show nodular structures very similar to those observed in CVD and electrolytically deposited films of other materials.¹⁰ The major feature of these

structures is that as can be seen in Fig. 7(a), the columnar growth commences in a direction that is not normal to the substrate surface and, as shown in Fig. 7(b) slowly changes toward the normal. The inverse of this structure, i.e., a hole in the film has also been observed. It is significant that the former structures, visible by virtue of the circular features they create in the film surface, have been observed in low defect density material.

FIGURE 7

(a) Transmission electron micrograph of nodular feature in 5%:25W:25°C film. (b) Scanning electron micrograph of nodular features in 5%:25W:230°C films.

Deposition Chemistry

To assist in understanding the nucleation and growth phenomenon, it would obviously be helpful to know what species are involved in this process and where the rate-limiting reaction occurs. A priori treatment of interactions of reactive plasmas with solids are notoriously difficult.¹¹ However a series of measurements of growth kinetics and examination of recent work in the area of silane photochemistry provide substantial clues to the specific case of silane decomposition. Previously reported studies⁵ of deposition rates in the parameter space just discussed found that at low R.F. power the deposition rate was independent of silane concentration over the range 0.1% to 100%. This was interpreted as indicating a surface-limited reaction. Although unpublished studies of Ar-SiH₄ ion-molecule reactions¹² throw doubt on the uniqueness of this interpretation, a study of the deposition rate as a function of dopant concentration does provide substantial support. Figure 8 shows the deposition rate of boron doped material under optimum (pure silane, low power) conditions for low defect concentrations plotted as a function of diborane concentration. The marked increase in deposition rate at a dopant concentration of only 1 part in 5000 is strongly reminiscent of the surface catalytic effects widely observed in plasma chemistry.¹³ The fact that a similar increase in deposition rate (using BCl₃) is seen in CVD deposition of a-Si:H,¹⁴ where the decomposition can only be a surface reaction, provides strong circumstantial evidence for the same situation in plasma deposition.

FIGURE 8
Deposition rate of a-Si:H:B films as a function of diborane/silane flow ratio.

FIGURE 9
Yield of disilane as a function of irradiation time in mercury-sensitized photolysis of silane (from E. R. Austin and F. W. Lampe, J. Phys. Chem. 80, 2811 (1976), reprinted with permission).

Having proposed that the film deposition can involve surface catalysis, it is interesting to find that there are well-established surface catalytic effects on the gas-phase products in photochemical reactions involving silane. Figure 9 shows the results of Austin and Lampe² on the yield of Si_2H_6 in mercury sensitized photolysis of silane carried out in cells with stainless steel and pyrex walls--the yield is obviously sensitive to the nature of the walls and even larger changes are observed when the walls are coated with an agent known to poison surface reactions.

A closer look at these results yields some even more fascinating information. Almost immediately after the onset of photolysis the cell window and the walls are coated with a layer of a-Si:H that steadily increases in thickness, yet the dependence of yield on cell wall material remains unchanged. This result implies directly that *the surface catalytic effects are transmitted through the a-Si:H film!* In view of the sensitivity of catalysis to both surface topology and defect sites we speculate that this effect and the luminescence reduction discussed earlier may be related. Two more results from this field that are equally interesting are that, (1) the decomposition reaction is reversible, atomic hydrogen will etch a-Si:H to produce SiH_4 ,^{2,15} and (2) from studies of both photolysis^{2,3} and electron impact dissociation,¹⁶ SiH_2 and SiH_3 seem to be the most likely candidates for surface reactants.

Hydrogen Environments and Physical and Chemical Stability

It was earlier suggested that a two-phase structure might be responsible for the fact that films with pronounced columnar structure were continuous and mechanically strong. Several pieces of evidence support this conclusion. The first, reported in earlier work,¹⁷ is a strong association between the 845 cm^{-1} mode (characteristic of $(\text{SiH}_2)_n$) and both defect state densities and the trends in morphology. Figure 4(b) shows the variation of a quantity related to the fraction of SiH_2 bound as $(\text{SiH}_2)_n$, over

the same parameter space shown in Fig. 4(a). More recently Reimer et al.¹⁸ have used free induction decay measurements of the proton nuclear spins to show directly that there is spatial inhomogeneity in the hydrogen distribution. Figure 10 shows Fourier transformed FID spectra for similar conditions to those in Fig. 1. Ancillary

FIGURE 10

Free induction decay spectra of protons in a-Si:H films prepared under different conditions.

experiments demonstrate that all spectra are dipole broadened leading to the conclusion that the two-line structure in the 5%:25watts:25°C sample arises from spatial inhomogeneity. Of particular interest is the fact that even in the 100%:2watts:230°C sample (7.8 at% H) the dipolar broadening is larger than predicted for a random distribution indicating clustering of monohydride species.

The different physical and chemical stabilities of samples prepared in different segments of the deposition space not only point to inhomogeneity associated with $(\text{SiH}_2)_n$ but reinforce the earlier results concerning substrate dependent effects. Detailed results concerning the hydrogen evolution are being presented elsewhere at this conference.¹⁹ The conclusions that have most impact on this discussion are that (1) material with columnar morphology shows rapid evolution of hydrogen coincident with the removal of $(\text{SiH}_2)_n$ as seen in I.R. spectra and (2) subsequent oxidation occurs producing Si-H and Si-O vibrational modes characteristic of hydrogenated SiO_2 . Even at temperatures significantly lower than the deposition temperature, oxidation and the destruction of $(\text{SiH}_2)_n$ are observed. It is concluded that the $(\text{SiH}_2)_n$ is physically located in the interstitial regions and that since the higher silanes are readily hydrolyzed and oxidized, oxidation proceeds rapidly in these regions and on the internal surfaces exposed by $(\text{SiH}_2)_n$ removal. This conclusion does not, however, rule out the possibility that a substantial fraction of the interstitial volume is empty, i.e., that there are anisotropic voids in the material. The rapid oxidation even without the removal of $(\text{SiH}_2)_n$ is suggestive of fast diffusion into interstitial regions.

Physical stability of films is a little discussed issue. It is characteristic of most thin films to possess considerable internal stresses. Amorphous Si:H films have, in our experience, more than their share. It is not uncommon to find fused silica substrates ~1mm thick totally fragmented by films ~1-5 μ thick, single crystal silicon slices visibly bowed and films peeling off metal electrode patterns but not off the uncoated substrate. It is found that the sign of the stress is strongly related to the morphology. All material with columnar morphology shows tensile stress that is typically weak--

large areas of $\sim 50\mu$ thick film can be removed whole from aluminium foil supports. In contrast, material deposited either with low R.F. power and high silane concentrations or on biased surfaces has compressive stress that, in general, increases with bias and is so strong that, coupled with the normal good adhesion of films, it can easily fracture substrates. It is significant that this behavior and its relationship to morphology, even to the effects of bias, is identical to that found in sputtered metal films by Thornton and co-workers^{20,21} where the columnar morphology originates from grain boundaries between crystallites. It is also significant that the models that exist to explain stress in thin films²² attribute the major effects to lattice parameter variations during the nucleation, growth and coalescence of islands. The fact that stresses are different on metal electrodes from those on fused silica thus provides indirect support for the earlier conclusions that the nucleation phenomenon is substrate material dependent.

DISCUSSION

Perhaps the most general conclusion that can be drawn from the structural studies presented here is that plasma-deposition is very similar to other thin film deposition techniques in terms of the structures it is capable of producing. Strongly anisotropic density fluctuations have long been considered as a major class of defects in thin films produced by a whole range of different techniques.²³ Magnetron sputtered polycrystalline metals,²¹ evaporated amorphous germanium,²⁴ sputtered amorphous silicon and germanium,²⁵ and some electrolytically deposited materials all possess this property. In addition the nodular structures produced by debris are very similar in appearance to those observed in the other techniques. Even the existence of a two phase structure is not unique. Recent work on plasma-polymerized hydrocarbons,²⁶ and D.C. sputtered molybdenum²⁷ has been interpreted in these terms. It is also not surprising to find that the nucleation phenomenon is substrate dependent--there are many reports in the literature of marked effects due to substrate morphology on the nucleation of thin films. There are however some features of the deposition process for the plasma-deposited films that are different from the counterparts in evaporation and sputtering. Barna et al.¹ showed that evaporated a-Ge possessed an island structure that had a two dimensional dendritic character. These authors modelled the growth process by assuming nucleation and growth via the capture of mobile adsorbed species--in that case atoms, on nuclei. They introduced an additional parameter, the mobility of the adsorbed species on the growing cluster, and imposed a general criterion for attachment, namely that the adsorbed atom would try to satisfy the maximum number of dangling bonds. With this model they found that a very low cluster-surface mobility produced dendritic growth (in 2D) while a high mobility produced a much more even island circumference. Based on this model, we conclude that a major difference between evaporation and plasma-deposition is enhanced surface mobility in the latter. We propose that the reason for this high mobility is that the diffusing species are probably SiH_3 and SiH_2 radicals. These have the property of having only one or two dangling bonds hence the strength of attachment to a surface site will be low and the mobility high. This proposal also naturally leads to the possibility of $(\text{SiH}_2)_n$ formation in the interstitial regions.

Independent of the details of the surface reactions it is clear that the transition from a dendritic to an approximately circular island circumference, by reducing the internal

surface area, will minimize the density of dangling bonds. In addition, it is seen that plasma deposition, for reasons we have yet to understand, permits island coalescence to be almost perfect under certain conditions providing a second improvement over evaporation. Although no microstructure can be resolved in the lowest defect density material, the substrate dependence of electronic properties and the surface ring structures indicate that nucleation and growth still produce some differentiation into columns and interstitial regions. We therefore propose the following model for growth of a-Si:H films. Substrate-dependent nucleation is followed by growth of islands until island boundaries are in close proximity. Depending on the surface chemical reactions and energy minimization considerations two extreme situations will arise. In the first an $(\text{SiH}_2)_n$ polymer phase forms that provides an elastic bond over at least part of the interfaces. Defects are probably located on or near these interfaces and residual stress in the structure is minimal. The second can be visualized initially in the absence of hydrogen as being the coalescence of a series of continuous random network structures of diameter $\sim 100\text{\AA}$. This will on an average create partly bridged interfaces with large numbers ($\sim 50\%$) dangling and strained bonds. Hydrogenation of these interfaces will result in the removal of the dangling bonds and probably scission of some of the more strained bonds but will still leave stress in the structure and an inhomogeneous distribution of both defects and hydrogen. It is important to recognize that this behavior can lead naturally to, (1) a higher average density of hydrogen than required to satisfy dangling bonds by a single random network structure, and (2) a non-unique relationship between hydrogen content and defect densities, biased in favor of lower hydrogen content in the least defective material.

There are still many unanswered questions about the growth of a-Si:H. Attempts to resolve the details of nucleation by TEM in very thin films have been unsuccessful due to the low atomic number of silicon--it may be that there is nucleation on a much finer scale followed by agglomeration of clusters.²⁸ There is also the problem of the origin of the isotropic small angle scattering in low temperature material and it is clear that a wider range of samples need to be examined by small-angle scattering and N.M.R. to determine in detail the effects of bias on the defect/hydrogen relationship. Doping also raises some interesting questions--300\AA thick p-n junctions of low defect density material show no structure in TEM, but doping does introduce defects and there is evidence²⁹ that $(\text{SiH}_2)_n$ modes appear as doping is increased to alloy levels with arsenic. Perhaps the progress can best be summarized by analogy to crystalline silicon--we have found the dislocations, now we have the point-defects in front of us.

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LUMINESCENCE AND ESR STUDIES OF DEFECTS IN HYDROGENATED
AMORPHOUS SILICON

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Abstract

New experimental information on luminescence and light induced ESR (LESR) in hydrogenated amorphous silicon is described. We demonstrate that the two experiments involve identical recombination transitions, and identify two separate processes. One process involves defect states, and from the doping dependence of LESR we deduce that the electronically active defects are dangling bonds with positive electronic correlation energy.

The nature of defect states in hydrogenated amorphous silicon (a-Si:H) has been the subject of much investigation and speculation. As in all other forms of a-Si, electron spin resonance (ESR) is observed at $g = 2.0055$ and is attributed (without clear proof) to dangling bonds.¹ However, an important discovery was that in a-Si:H samples, particularly when doped, the ESR spin density can be much larger during illumination than in equilibrium, and this property led to the suggestion of defects with a negative effective correlation energy U .^{2,3} Subsequent defect structures proposed include divacancies,⁴ twofold coordinated Si atoms,⁵ negative U three-center-bonds,⁶ pairs of negative U defects,^{5,7} and reconstructed inner surfaces.⁸ This Letter describes new experimental information about the nature of defects in a-Si:H. We identify a relation between luminescence and light induced ESR (LESER) from which we argue that positive U dangling bond defects predominate.

The samples used were prepared by plasma decomposition of SiH_4 , with the deposition conditions chosen to give equilibrium spin densities of $3 \times 10^{15} - 10^{17} \text{ cm}^{-3}$ in undoped samples.⁹ Undoped a-Si:H at low temperature has a broad luminescence band near 1.4 eV (see Fig. 1a) with a high quantum efficiency if the spin density is $< 3 \times 10^{17} \text{ cm}^{-3}$.⁹ In moderately doped n- or p-type samples there is also a weaker luminescence band at 0.9 eV¹⁰ which is sometimes seen in undoped samples with a spin density of about 10^{18} cm^{-3} .¹¹ From its independence of doping type, the 0.9 eV luminescence evidently arises from recombination at native defects rather than at impurities. Figure 1b shows a schematic energy diagram¹¹. The 1.4 eV luminescence is attributed to transition A between band tails.⁹ Singly occupied defects quench this luminescence⁹ by tunnelling of the electron into the defect (transition B).¹² Since the 0.9 eV band is only observed when the 1.4 eV luminescence is strongly quenched, the most plausible mechanism is the recombination of the trapped electron and a tail state hole (transition C).¹¹

Figure 2 shows LESR spectra at 30K of doped and undoped a-Si:H samples. N-type samples have a single resonance of width 7.5G at $g = 2.0055$, whilst p-type samples have an additional broad (~ 20 G) line at $g \sim 2.013$, in agreement with previous results.² The undoped samples also show two resonances. One is the same broad line, but the second is not the usual 7.5G line at $g=2.0055$. Instead it has a width of about 6G and a lower g-value (2.004).

The distinction between the LESR of doped and undoped samples is important, and is clearly demonstrated by its relation to the two luminescence bands. Figure 3 shows the temperature dependence of LESR and luminescence. Both doped samples have the same dependence of LESR within the experimental uncertainty, and in the p-type material, both resonances have the same behavior. Of particular significance is that between 100K and 300K the 0.9 eV luminescence intensity shares the same temperature dependence. In undoped material LESR quenches at a distinctly lower temperature, but with an identical dependence as the mean lifetime of 1.4 eV luminescence (see Fig. 3).

Luminescence is generally described as a competition between a radiative rate P_r and a non-radiative rate P_{nr} , such that the efficiency y_L and the lifetime τ are given by

$$y_L = P_r / (P_r + P_{nr}) . \quad (1)$$

$$\tau = 1 / (P_r + P_{nr}) . \quad (2)$$

LESR is observed when absorbed photons create singly occupied states. If the generation rate of such states is G and the same recombination processes are assumed, then the LESR spin density N is given by

$$N = G / (P_r + P_{nr}) = G\tau = Gy_L / P_r \quad (3)$$

The identical temperature dependence of τ and N in undoped material (Fig. 3) clearly demonstrates that the same recombination mechanisms do indeed apply to both experiments. We therefore conclude that the same excited states are involved. A similar result for LESR and 0.9 eV luminescence in doped material is deduced from the temperature dependence of y_L and N between 100K and 300K. (The lifetime of 0.9 eV luminescence is experimentally difficult to obtain). The divergence of y_L and N below ~ 100 K in both cases (Fig. 3) is evidently due to a temperature dependence of P_r (see eq. 3), as is known to occur in undoped samples.¹²

Three other properties confirm the relation between the luminescence and LESR recombination processes. Firstly, both the 0.9 eV luminescence and LESR are progressively quenched when the doping level exceeds about 10^{-3} . Secondly, sub-band-gap illumination (< 1.7 eV) excites the 0.9 eV luminescence, but not that at 1.4 eV, and also results in LESR in doped material but not in undoped. We attribute this result to extrinsic absorption at defects. Thirdly, in undoped samples of increasing equilibrium spin density, obtained by varying the deposition conditions,⁹ both the 1.4 eV luminescence and the LESR decrease.

The conclusion that luminescence and LESR involve the same recombination mechanisms clarifies the origin of the observed LESR resonances based on the identification of the luminescence recombination shown in Fig. 1b. The broad resonance at $g \sim 2.013$ is identified as band tail holes, and this result is supported by observations of this line in equilibrium ESR in p-type samples, and in its absence in n-type samples.¹³ The 7.5G line at $g = 2.0055$ is the singly occupied defect and the narrower $g = 2.004$ resonance is that of electrons in the conduction band tail. Again, these results are supported by other equilibrium ESR observations.^{1,14}

We now relate these results to the defect structure. The spin properties of any point defect can be categorized as one of three types. The first contains an odd number of electrons when neutral, has a positive correlation energy U , and is typified by a dangling bond. This defect has an unpaired spin when neutral, but does not exhibit ESR when singly charged either positive or negative. A second positive U defect has an even number of electrons when neutral, as in the crystalline silicon divacancy. This center can be observed by ESR only in either its positive or negative singly charged states (which in general have different ESR spectra). By moving the Fermi energy sufficiently both these types of defects will occupy their various charge states in equilibrium. Positive LESR is observed when the equilibrium state has paired electrons (or is empty) and when optical excitation can change the occupancy. The third type of defect has a negative U as postulated for chalcogenide glasses³. In equilibrium at low enough temperature, such defects are either doubly occupied or empty. ESR from the singly occupied state is only observed by excitation out of equilibrium, irrespective of doping.

Figure 4 shows schematically the expected doping dependence of equilibrium and light induced ESR for defects of the three types. Each type has a characteristic, and qualitatively quite different behavior. The curves are based on the following assumptions: 1) donor and acceptor levels are shallow¹⁵ so that excess carriers transfer to defect states; 2) LESR arises from defects which are initially either doubly occupied or empty; 3) rapid non-radiative recombination quenches LESR at high doping levels (see eq. 2).⁹ Changes in defect density with doping¹⁶ do not affect the results qualitatively because only the *relative* magnitudes of equilibrium ESR and LESR are important to the discussion. Also shown in Fig. 4 is the variation of band edge LESR which, from Eq. 1 and 2, we expect to vary with the luminescence efficiency, and therefore to decrease with doping.¹⁶

Our identification of the separate band edge and defect LESR components in Fig. 2 shows that defect LESR is only observed in doped samples. From the data of Fig. 2 and ref. 2 and studies of other undoped samples of varying equilibrium spin density, we conclude that the equilibrium *defect* spin density is larger than that of LESR in undoped samples, but smaller in doped samples. Thus our data are fully consistent with defects of the first type in Fig. 4, but are clearly opposite to the expectations for the even defect. Furthermore the negative U model cannot explain either the zero doping minimum in LESR or the observations of an equilibrium spin in undoped samples. (These properties of the undoped samples highlight the different behavior of a-Si:H compared to chalcogenide glasses.)

Of all the defect models proposed,¹⁻⁸ only the dangling bond is of the correct spin type. The dangling bond is structurally the simplest of all the defects, and it is difficult to conceive a neutral, singly occupied defect that does not involve a dangling bond. This assignment is further corroborated by the constancy of the g -value in a-Si prepared in differing ways, which suggests a fairly localized electronic wave function. Our results obviously give only indirect information about the gross atomic structure of the defect. However the data are consistent with the model of a dangling bond on an incompletely hydrogenated (or reconstructed) void surface.

In summary, our LESR measurements strongly indicate that the primary defects in a-Si:H are positive U dangling bonds. Furthermore the association between LESR and luminescence allows us to confirm previous recombination models, as well as to clarify the origin of all the LESR spectra.

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Figure Captions

Fig. 1 a) Luminescence spectra of doped and undoped a-Si:H. b) Schematic energy diagram showing band tail states, the two electronic states of the defect and possible transitions as described in the text. (From ref. 11). The energies of the radiative transitions A and C refer to the luminescence peak position.

Fig. 2 LESR spectra of doped and undoped a-Si:H. Equilibrium ESR is negligible in all three samples. Note the g-value shift in undoped samples.

Fig. 3 Temperature dependence of LESR spin density compared to the luminescence intensity of the 0.9 eV and 1.4 eV bands, and the mean lifetime of the 1.4 eV band, in doped and undoped a-Si:H.

Fig. 4 Schematic diagram of the predicted doping dependence of the various ESR lines for three different defect types described in the text.

FIG 1

LESR a-Si:H

30K

9 GHz

0.001 mW

$E_x = 1.915$ eV

100 mW/cm²

FIG 2

FIG 3

FIG 4