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Improved electrical properties of non-hydrogenated a-Si densified by IBAD

D C Craigen† and D E Brodie
Guelph–Waterloo Program for Graduate Work in Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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Abstract. Some effects of ion bombardment on the growth of non-hydrogenated amorphous silicon films were studied using samples prepared with low-energy ion-beam-assisted deposition (IBAD). Inert gas ions were used to determine the effects of the ion beam on pure amorphous silicon without the complication of simultaneous chemical effects. The ion bombardment was found to increase the film density, improve film stability, increase the effective conductivity activation energies and to move the position of the infrared absorption peak assigned to silicon–carbon bonds to larger wavenumbers. The largest effective conductivity activation energies and the lowest conductivities were obtained from films made with Ar^+ ions and bombarding energies around 100 eV. However, these 'best' films still do not have a sufficiently low defect density to be useful semiconductors. The improvements are consistent with the thesis that densification of the growing film is the primary effect of the beam. However, for the conditions used, the densification appears to saturate, leaving a relatively large number of dangling bonds in the films. These may result from the presence of Ar known to be in the films, although the results are consistent with the topological model which suggests that the best conditions for forming covalently bonded solids are obtained when the number of bonding constraints is equal to the number of degrees of freedom.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) is a widely studied semiconductor because of its potential importance for many technologies [1, 2]. Pure a-Si has been studied extensively, but it has not been useful because its electrical properties are dominated by a very high defect density [3]. There are many inconsistencies in the reported properties of this material for two main reasons: (1) the properties of the films are very sensitive to the fabrication process [4] and (2) in many cases there is inadvertent incorporation of hydrogen (or other impurities) into the growing film. Since the effects of hydrogen became known, there have been very few attempts made to produce useful non-hydrogenated a-Si. While the hydrogen is thought to be necessary to achieve high quality films, it may also be responsible for the instabilities observed, especially the Staebler–Wronski effect [5].

Polk's mechanical model [6] for covalently bonded materials suggests that an ideal random network for a-Si should be possible, in principle. Steinhardt *et al* [7] have considered two elastic-energy-relaxed continuous-random-network (Polk) models for

† Present address: Department of Physics, Acadia University, Wolfville, Nova Scotia, Canada B0P 1X0.

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tetrahedrally bonded amorphous semiconductors. They found that the density of this material is within 1% of that of a diamond cubic lattice and for a reasonable value of the bond bending force constant, RMS bond length distortions of about 1% are obtained and bond angle distortions are about 7.0°. The main defects in real non-hydrogenated a-Si are believed to be due to three-fold coordinated neutral silicon atoms, i.e. dangling bonds, mainly on the surfaces of microvoids and cracks. If models like these [6, 7] represent possible real structures, one might expect to obtain a more ideal random-network structure by depositing well annealed high density films.

On the other hand, Phillips [8] has discussed a topological atomic model which indicates that the best conditions for forming disordered covalently bonded solids occurs when the number of bonding constraints is equal to the number of degrees of freedom (the number of dimensions), i.e.

$$\begin{aligned}\{\text{the number of degrees of freedom}\} &= \{\text{the number of constraints/atom}\} \\ &= \{\text{average number of bonds/atom}\} \\ &\quad + \{\text{average number of bond angles/atom}\} \\ &= m/2 + m(m-1)/2 = m^2/2\end{aligned}$$

where m is the average number of nearest neighbours per atom. In the case of three-dimensional space this yields: $m^2/2 = 3$ or $m = 6^{1/2} \approx 2.45$.

Pure a-Si, with $m = 4$, is 'overconstrained', and coordination defects form during film growth to relieve film stress by reducing the coordination number. This model can explain the observation that a-Si normally contains large densities of dangling bonds and hence, the fact that it does not appear to be possible to make an a-Si ideal random network. Given the potential usefulness of achieving an ideal random network for a-Si, and since a method is available that can produce high density films, it is appropriate that one try to check directly the validity of this model.

More recently, Phillips *et al* [9] have studied the submicrostructure of 'amorphous' silicon. The growth of the films on clean crystalline substrates was expected to induce improved morphological order throughout the pure amorphous film. They used high-resolution transmission electron microscopy and the observations support a submicrocrystalline model for the structure of non-crystalline solids.

Except for sputtering, the deposition techniques used for fabricating pure a-Si have not involved the use of ion bombardment. On the other hand a-Si:H is often prepared with ion bombardment present. In many cases it is an intrinsic part of a deposition process that is not suitable for producing pure a-Si, and the method makes it difficult to isolate the physical effects of the ion beam as well as the different ion beam parameters. Within limits, ion-beam-assisted deposition (IBAD) permits independent control of all of the deposition parameters for the fabrication of a film. In this technique, the film is deposited from an atom vapour beam, while the substrate is bombarded by an ion beam, each from a different source. Under the appropriate conditions the ion beam is known to be able to alter many properties of a growing film [10, 11] and in particular, can increase the film density as well as reduce film stress. If the presence of dangling bonds can be reduced significantly for these materials, an ion beam with the correct parameters and deposition conditions might be able to maximize the film density and thus minimize the number of dangling bonds needed.

If defect-free a-Si in the form of an ideal random network could be made, the Fermi level should be near mid-gap resulting in an electrical activation energy of approximately 0.6 eV. However, due to the high density of coordination defects, the dominant conductivity mechanism in a-Si at low to moderate temperatures is hopping via localized defect states and the log σ versus $(1/T)$ curve is not linear. However, the tangent to this curve at any particular temperature, can be used to define an effective activation energy at that temperature. For vacuum deposited a-Si, this effective activation energy is approximately 0.15 eV at room temperature [12]. Activated extended-state conduction becomes the dominant conductivity mechanism at high temperatures (> 200 °C for pure a-Si). It was expected that as the defect density is reduced the 'effective activation energies' would increase, the conductivity would decrease, and the temperature at which activated conduction becomes dominant, would be lowered.

One of the earliest attempts to produce good quality a-Si in an ideal random-network structure, without hydrogen, was reported by Fane [13], and that involved the use of a light inert gas (neon) to sputter Si. Some success was reported but the author did not comment on the possible hydrogen content in the films due to the possible presence of water vapour in the sputtering system. Brodie and Moore [14] attempted to influence the structure of vacuum deposited a-Si:C by bombarding the growing film with relatively low energy electrons, but in that case, water vapour was freed from the chamber surfaces by the electron beam and hydrogen was incorporated into the growing films [14].

Ion bombardment of growing a-Si:H and a-SiN_x:H has been used by a few authors in order to try to influence the H bonding configurations and obtain device grade materials [14–20], to calibrate the IBAD method for depositing a-SiN_x:H [21, 22] or to improve the properties of these films [23]. We are aware of no work that has been done using low-energy ion beams and the IBAD technique to try to achieve an ideal random-network structure for non-hydrogenated pure a-Si.

In this study, the objective was to use the independent control over the parameters (in the ranges available) allowed by the IBAD system to re-examine the extent to which the coordination defect density in a-Si could be lowered without hydrogen and hence achieve a more ideal random-network structure in this potentially important material.

2. Experimental details

The deposition system consisted of an 18 inch glass cylinder pumped with a six inch oil (corning 705 oil) diffusion pump, a LN long life trap and two 600 W bakeout lamps. When minimum water vapour in the system was needed, it was necessary to bake the system for at least two days prior to depositing the sample.

Pressures were measured with both a nude ion gauge and a Hiden residual gas analyser mounted in the chamber. Viton was used to seal the glass cylinder and all other seals in the system were metal.

A neutralized ion beam was provided by a Kaufman-type broad-beam source, manufactured by Ion Tech. Inert-gas ions were specifically chosen in order to eliminate possible chemical effects of the ion-beam species. The ratio of the ion to atom arrival rates at the substrate was varied from 0.3 to 16 (a ratio of 0 implies no ion beam was used), the inert-gas ion masses tried were 4, 20, 40, and 84, and the ion energies were controlled by varying the ion beam voltage from 30 to 300 volts.

These ion-beam voltages also give the average ion energies with a spread of about 15 eV.

Control samples were made using approximately the same deposition rate ($\approx$ 0.1 nm s^{-1}) as that for the 120 eV ion-bombarded samples, but without ion bombardment. All samples were deposited onto substrates held at $\approx$ 214 °C and the completed films were annealed at that temperature for 30 minutes before beginning the conductivity measurements. When deposition conditions were reproduced, variations of approximately 10% from the mean values of the room-temperature conductivities and the high-temperature effective activation energies were obtained, and this is indicative of the reproducibility of samples. Silicon was evaporated from either an electron-beam source or a resistively heated vitreous carbon crucible. The vitreous carbon source always introduced about 1 at.% carbon into the films and this was the only impurity that could be detected in the IR spectra for the non-hydrogenated samples.

Basic pressures of less than 10^{-6} Pa ($\approx 10^{-8}$ Torr) were achieved, and the water vapour partial pressure was always reduced below 6×10^{-7} Pa before the films were deposited. With the exception of a few samples made with Ar present in the system, the non-hydrogenated control samples (i.e. no ion bombardment) were made with a maximum residual gas pressure during deposition of 2.6×10^{-6} Pa, and the water vapour pressure remained below 10^{-6} Pa. Under these conditions it has been shown [14] that the water vapour present during growth has no effect on the electrical properties of evaporated a-Si. Films were made from 100 to 600 nm thick with most around 350 nm.

Three samples were analysed by Rutherford back scattering (RBS) and particle-induced x-ray excitation (PIXE) in order to determine sample purity and to estimate the density of the three types of films studied. These included a reference sample made with Ar in the system but no ion beam, a slowly deposited (0.005 nm s^{-1}) sample that was bombarded during growth with 30 eV Ar ions, and a sample deposited at a faster rate (0.1 nm s^{-1}) and bombarded with 120 eV Ar ions during growth.

The reference samples contained $\approx$ 1 at.% C and the one made in an Ar atmosphere also contained $\approx$ 0.4 at.% Ar. The sample deposited at a slow rate and bombarded with 30 eV ions contained a trace of Fe and As as well as C and $\approx$ 9 at.% Ar. The sample deposited at the faster rate and bombarded with 120 eV ions contained carbon and a trace of a heavy element near gold, uniformly distributed through the sample, as well as $\approx$ 8 at.% Ar.

Electrical conductivity was measured (*in situ* following the standard anneal) as a function of temperature using a planar geometry. Films used for electrical conductivity measurements were deposited onto Corning 7059 glass substrates and, at the same time, samples used for infrared spectroscopy were deposited onto polished crystalline silicon wafers attached to one corner of the glass substrate. Infrared absorption measurements were made as soon as the samples were taken from the vacuum system, using a Perkin-Elmer 983 spectrophotometer.

3. Results

3.1. Electrical properties of a-Si

Figure 1 illustrates the different temperature dependences observed for amorphous silicon films: (1) represents a pure a-Si film which was vacuum-deposited in a good

vacuum without ion-beam assistance, (3) represents a film containing some hydrogen (it was reactively deposited in an atmosphere of $\approx 5\times10^{-6}$ Pa of water vapour with no ion-beam assistance [14]), and (4) represents a film which contained more hydrogen (it was deposited reactively in a partial pressure of water vapour set at $\approx 5\times10^{-5}$ Pa, without ion beam assistance). (2) illustrates the conductivity $\sigma(T)$ observed for an a-Si film made with ion-beam assistance in the system when the partial pressure of water vapour was reduced to the minimum possible. For curves (1) and (2), the non-hydrogenated samples, the conductivity is dominated by hopping in this temperature range. For a slightly hydrogenated sample, a transition from hopping to extended-state conduction is observed near $1000/T \approx 2$, or ≈ 100 °C. As the defect density is further reduced by the addition of more hydrogen, the hopping conductivity is reduced more and only extended-state conduction is observed. Figure 1 shows the effect of hydrogen on the conductivity of an a-Si film and where a typical ion-bombarded film fits in relation to these. All of the a-Si samples made in this study, using IBAD and no hydrogen, had electrical conductivities which ranged between the non-hydrogenated (1) and the slightly hydrogenated (3) samples. Because the addition of hydrogen is known to reduce the defect density in a-Si, and the $\sigma(T)$ curves change as given in figure 1, either decreases in the conductivity or increases in the slope of the log σ versus $(1/T)$ curve (i.e. increases in the effective activation energy) are taken as indications of a reduction in the relevant gap-state defect density.

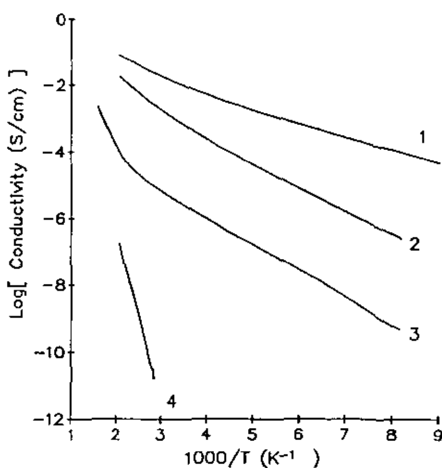

Figure 1. The temperature dependence of the electrical conductivity for (1) a non-hydrogenated and non-ion-bombarded a-Si sample, (2) a non-hydrogenated and Ar^+ bombarded sample, (3) a slightly hydrogenated non-bombarded sample, and (4) an a-Si:H sample.

A series of samples was prepared with a varying Ar^+ ion to Si atom ratio (0.3 to 16) in the vapour beam, a fixed ion-beam energy of 120 eV (figures 3, 4 and 5 justify these choices) and the fast (0.1 nm s^{-1}) deposition rate. Figure 2 shows the changes observed in the slope of the log $\sigma(1/T)$ curve, where the effective high-temperature activation energy E_{ah} (measured at 200 °C) is plotted for these samples (*), for a few samples (x) made with a lower ion beam energy (30 eV) and the much slower

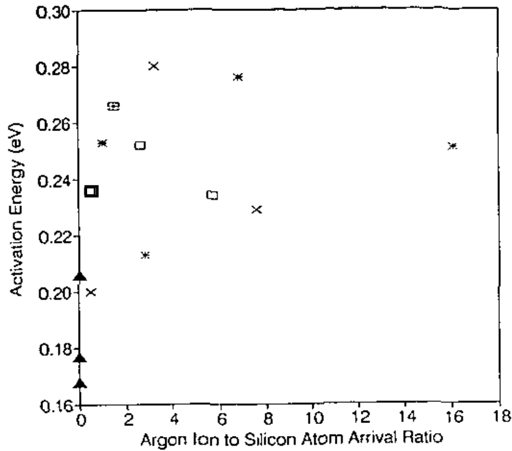

Figure 2. High-temperature effective activation energies (≈ 200 °C) are plotted as a function of the ratio of the Ar^+-ion arrival rate to the Si-atom arrival rate at the substrate. ▲, control samples; x, 30 eV Ar^+ ions; *, 120 eV Ar^+ ions; □, Ar^+ ions with ion energies between 30 and 120 eV and the same substrate temperature, 214 °C.

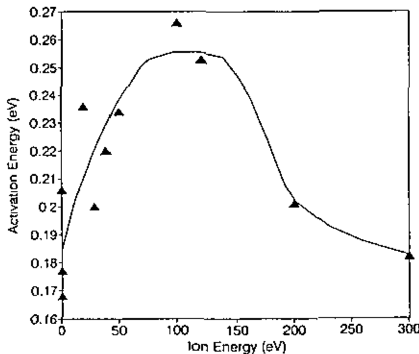

Figure 3. High-temperature effective activation energies versus ion energy using Ar^+ ions.

(0.005 nm s^{-1}) deposition rate, and four additional samples (□) made with beam voltages varying between 30 and 120 eV but made at the same substrate temperature of 214 °C.

When ion bombardment is used, the slopes generally increase and the room temperature conductivities decrease, even with small ion-to-atom ratios, but the improvements saturate near ratios of 2 or 3. The control sample with the lowest E_{ah} (≈ 0.17 eV, shown in figure 2) obtained for the group of samples made at the fast deposition rate, was deposited with argon in the chamber, the ion source activated, but no ion beam extracted, i.e. no ion-beam voltage applied. Under these conditions the ion-beam current is zero. On the other hand, the control sample which gave the highest E_{ah} (≈ 0.20 eV) was obtained in a good vacuum. These results suggest that no reactive gases capable of removing defects (e.g. hydrogen or water vapour) are being inadvertently introduced into the deposition chamber along with the argon, and

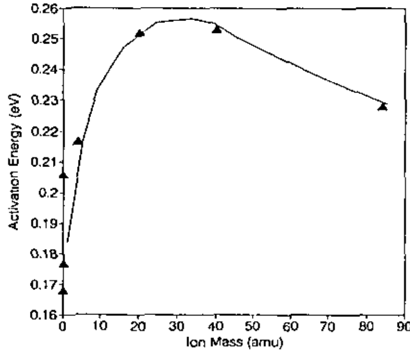

Figure 4. High-temperature effective activation energies versus ion mass. 0 indicates no ion beam; masses of 4 amu (He ions), 20 amu (Ne ions), 40 amu (Ar ions) and 84 amu (Kr ions).

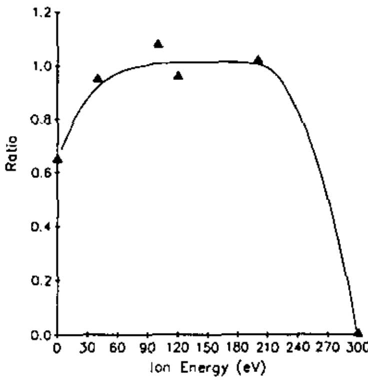

Figure 5. Ion-energy dependence of the ratio of the conductivity measured after several months of exposure to the laboratory ambient to the sample's initial conductivity, i.e. the film stability.

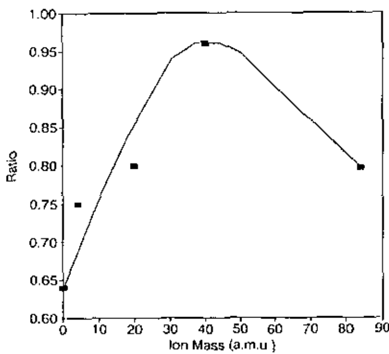

Figure 6. The dependence of the film stability on the mass of the ions used in the IBAD process. Ion masses are the same as those indicated in figure 4.

this result is consistent with data given by the residual-gas analyser when checked with lower Ar pressures in the system.

For the samples made using the lower ion-beam energies (30 eV) and because the source yields a very low ion-beam intensity at these low energies, larger ion-to-atom ratios could only be obtained by reducing the deposition rate. One control sample was made at this slow deposition rate (0.005 nm s^{-1}) and it yielded an E_{ah} of only 0.11 eV as well as a larger room-temperature dark conductivity. Under these conditions, these samples could have more of the residual gases incorporated into the film, and any of the reactive species present (like water vapour) would be expected to increase E_{ah} and decrease the conductivity. Since this did not happen, one might speculate that at these very low deposition rates, the mobilities of the adatoms were such that a more disordered film was produced. This would suggest that ion-beam-assisted deposition yields the largest improvement in the structure and thus the electrical properties, for films prepared under these conditions. However, even these 'good' film properties were no better than those obtained using the faster deposition rates (see figure 2). If the larger increase in E_{ah} is due to a bigger improvement in the structure of these samples introduced by using ion-beam energies near 30 eV, this would suggest that the lowest defect density in a-Si (made using IBAD) might be obtained with very large ion-to-atom ratios and very low energies. It should be noted that no photoconductivity was detected in any of these non-hydrogenated films.

The dependence of E_{ah} on the ion-beam energies between 30 and 300 eV is given in figure 3, for Ar^+ ions and ion-to-atom beam ratios near 3. In this case, the optimum beam energies occur for a range from 90 to 120 eV. At lower energies, either the scouring effect of the beam may be too little or the ion-to-atom ratio is not large enough, while the higher energy ions appear to penetrate too far and generate deeper defects that do not anneal.

In order to observe the effect of changing the ion mass when 120 eV ions are used, four different inert-gas ions were tried: helium, neon, argon and krypton. The results are illustrated in figure 4. In all cases, E_{ah} was larger when the ion beam was used than it was for the control samples. The largest improvement in this parameter was obtained when the maximum momentum transfer occurred, i.e. when the ion mass was closest to the mass of the silicon atom (i.e. Ne and Ar). At least for 120 eV ions, this suggests a significant role for momentum transfer to the surface adatoms during the interactions of the ion beam with the growing film. For a given set of deposition parameters, this condition would be expected to provide maximum densification in the growing film through forward recoils and consequently, a structure a little closer to an ideal random network with fewer or smaller voids, providing the ion energies are not too large. This is consistent with simulated results of the IBAD process that have been obtained through modelling. For example, many of the effects of low-energy ion bombardment (below $\approx$ 200 eV) have been reproduced by modelling [24]. In particular, a Monte Carlo model has been developed [25] which considers the effect of ion-assisted deposition on microscopic void structures in a growing film. The ion beam causes knock-ons to fill the voids and increase the film density. This has been shown to correlate well with some experimental results [25].

However, in our case the effect of the ion beam on the electrical properties of these films is complicated by the presence of Ar in the bombarded films in concentrations of Ar/Si of 0.08 to 0.09 for both 30 and 120 eV energy ions, determined by RBS and PIXE. These impurities must introduce some minimum number of dangling bonds and could be responsible for the apparent limit in the improvement in the

structure and the observed electrical properties. At the same time, the improvement in the films observed when an ion beam is used must come from the densification effects of the ion beam. Film thicknesses were measured using a Talysurf profilometer and the atom areal densities for the three films noted earlier were measured by RBS. The densities of the three films were determined to be 2.10 ± 0.05, 2.16 ± 0.06, and 2.38 ± 0.1 g cm^{-3} for the reference film, the film made with 30 eV ions, and the film made with 120 eV ions, respectively. Crystalline silicon has a density of 2.3296 g cm^{-3}.

3.2. Stability of a-Si

Studies of a-Si:H [20] and a-SiN_x:H [23] have demonstrated that porous films will gain oxygen (shown by IR spectra) after exposure to the laboratory environment. The electrical properties of such films change simultaneously.

Films prepared using IBAD for this study show no changes in the IR oxygen-related absorption even after several months. However, some show changes in their electrical properties. The void surfaces in this non-hydrogenated a-Si do not appear to be accessible to oxygen; however, in a few cases, small amounts of bonded hydrogen can be detected later that could not be detected initially in the IR spectrum and would account for the observed decrease with time in the room-temperature conductivity. Figures 5 and 6 illustrate the effects over time of ion energy and ion mass on the stability of the electrical properties of the resulting films. The ion-to-atom arrival ratios were approximately 3 for these samples. Stability was indicated by measuring the ratio of the room-temperature electrical conductivity as it ages to the initial value. A ratio of 1 corresponds to a stable film. This ratio increases from ≈ 0.6 as the Ar^+ ion-beam energy increases from 0 (no ion bombardment), with a broad maximum value near 1, centred around beam energies of 120 eV. Note the film made with a 300 eV beam energy is the least stable. The stability shows the same dependence on ion energy and ion mass as E_{ah} did, suggesting that the mechanism which increases the stability is the same mechanism that increases E_{ah}.

3.3. Bonding configurations of carbon impurities

When films were deposited from a resistively heated vitreous carbon crucible, they exhibited a small IR absorption peak at 700–750 cm^{-1}. In general, this peak shifts toward higher wavenumbers with increasing ion energy for a fixed ion-beam current. This particular peak was not seen when the electron-gun source was used to evaporate Si, and thus we assume that it is Si–C related, with the carbon coming primarily from the carbon crucible. A shift in the position of a similar peak in a-$Si_{1-x}C_x$:H has been interpreted as being due to a mixing of the Si–C (≈ 700 cm^{-1}) and Si–CH_3 (780 cm^{-1}) peaks [26]. CH_3 may be present in our films because two much smaller peaks near 780 and 1250 cm^{-1} are often observed together, even in films deposited using an electron-gun source. This pair of peaks is generally accepted as being due to CH_3 [26]. CH_3 is probably being incorporated into the films through a reaction of the growing film surface with ambient hydrocarbons. These are known to be present at very small partial pressures, since they can be detected with the residual gas analyser as components of the base pressure gases in the deposition chamber. However, since small CH_3 peaks are observed independently of the presence of the Si–C peak being discussed, the shifting of this peak is probably not due to mixing with a Si–CH_3 peak. Borders *et al* [27] have reported that the Si–C mode found at 700 cm^{-1} in amorphous

unhydrogenated Si–C shifts to 800 cm^{-1} upon crystallization. Consequently, we are suggesting that for our samples, the shift in this Si–C IR peak to higher wavenumbers is due to more ordered carbon bonding which results from interactions between the ion beam and the growing film surface.

4. Discussion of pure a-Si

The RBS measurements indicate that some IBAD samples have an increased density (approaching that of crystalline Si) and this is corroborated by the improved stability noted for these samples as well as the shift in the carbon–silicon peak toward its crystalline value (800 cm^{-1}).

It is expected that since higher-density films have less effective surface area, they will be more electrically stable when exposed to the laboratory environment. Further, since the electrical transport is probably occurring near the Fermi level in these samples and because bombarded-sample conductivities change in the same way as do samples to which some hydrogen has been added (see figure 1), it is assumed that a decrease in the room-temperature conductivity and an increase in the effective conductivity activation energy implies a decrease in the density of defects near the Fermi level. As discussed above, the ion beam promotes a higher-density film at moderate energies due to forward recoils of surface atoms into any voids or cracks in the film surface. This should result in fewer and/or smaller microvoids, and hence fewer dangling bonds. The coincidence of the higher effective activation energies with stable material suggests that the removal of some voids is the reason for the small reduction in the defect density. Since this effect saturates it is tempting to speculate that while the ion beam is effective in removing microcracks and larger voids, it does not appear to be removing them and their related dangling bonds completely. This would be consistent with the suggestion that an intrinsic dangling-bond density, probably associated with microvoids, is needed to relieve strain in this overly constrained material [8]. These results would be consistent with the hypothesis [8] that it may not be possible to produce hydrogen-free, low defect-density a-Si. Unfortunately, the presence of a large concentration of Ar in these bombarded films could be responsible for a dangling-bond density that would make that conclusion less convincing. The insertion of Ar into the bombarded films suggests that the IBAD process, for the range of parameters used in this study, does not provide a definitive test for the strain-relief hypothesis discussed by Phillips [8].

Energetic beams in a deposition chamber can lead to an increased inclusion of impurities. The beam may enhance the incorporation of light-mass impurities from residual gases or it may further outgas any surfaces it hits, leading to a higher partial pressure for some gases than was present without the ion beam. In either case, this could lead to an increase in the hydrogen and/or oxygen content in the film. This would provide an alternative explanation for the increase in the effective activation energy with the use of the ion beam. Since the hydrogen content of these films is too small to be measured with IR spectroscopy we are unable to conclusively show that this is not the case. To minimize this possibility, all shielding and particularly that which may be hit by the ion beam, was degassed by heating them to $\approx 100\,°C$ for several days before the deposition, and as a result, there was very little or no change noted in the partial pressures of H_2 or H_2O when the ion beam was turned on. If the effects reported here were due only to outgassing, it is difficult to explain

the variations observed for the different ion masses, ion energies and the ion-to-atom ratios used.

5. Conclusions

The IBAD process is able to make non-hydrogenated a-Si films with improved electrical properties compared to those observed for vacuum-deposited a-Si. The main effect of the ion beam on the resulting film is the growth of a higher density material. However, the range of ion-beam parameters used in these experiments did not produce device-grade films. On the other hand, films that contain ≈ 9 at.% Ar cannot be expected to be device quality.

The increased density yields an improved structure as shown by the stability measurements. Since the electrical resistivity and the effective activation energies of these 'improved' a-Si films remain much lower than those obtained for a-Si:H, it is clear that a large number of defects remain and an ideal random-network structure was not achieved. The Ar content in the bombarded films could be responsible for a residual dangling-bond density and thus prevent the formation of an ideal random network. In any case, no results were obtained that would enable us to question Phillips' suggestion that a minimum density of dangling bonds is required in a-Si to reduce the strain energy in this otherwise overconstrained material.

Acknowledgments

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