Presented at the 6th Conf. on Application of Accelerators in Research & Industry November 4, 1980, Denton, TX Published by IEEE, Apr. 1981 Transactions on Nuclear Science

THE HYDROGEN CONTENT OF MULTICOMPONENT AMORPHOUS SILICON ALLOYS BY ^{19}F NUCLEAR REACTION ANALYSIS

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Summary

Chemical vapor deposited (CVD) amorphous silicon alloyed with carbon or nitrogen (α-Si:X, X=C or N) to retard high temperature crystallization is a promising absorber material for photothermal solar energy conversion. Films are prepared by decomposing silane containing gas mixures, a technique which is known to incorporate hydrogen into α-Si in some cases. Using the 16.45 MeV resonance of the $^{1}H(^{19}F,\alpha\gamma)^{16}O$ reaction we made the first measurements of the hydrogen incorporation in CVD a-Si:X films (X=C,N). We have made three observations. First, the incorporation efficiency of hydrogen into CVD a-Si increases by a factor of twenty as the carbon content increases from 0 to 35 atomic percent which indicates that previous studies of multicomponent systems may need to be reevaluated since this enhancement in incorporation efficiency involves hydrogen--a key alloyant in a-Si. Second, the quantity of hydrogen incorporated increases at a greater than linear rate as a function of carbon content which implies that the presence of hydrogen in the films is not accidental but is a necessary part of film growth. Third, the hydrogen content of a-Si decreases to almost zero after high temperature anneal which may help explain reported shift in optical constants.

Introduction

Amorphous materials containing silicon are promising materials for photovoltaic and photothermal solar energy conversion.[1-4] It has been found that the optical, electronic and structural properties of amorphous materials can be modified and often improved by alloying with one or a number of elements including, for example, H, B, C, N, O, F, P, Si, Ge or a number of transition elements.[3-7]

In the case of alloys which are based primarily on silicon, amorphous silicon-hydrogen alloys (often abbreviated, a-Si:H) are one of the earliest known and remain among the best studied two-component systems. It is worth noting that in the first a-Si:H films produced, hydrogen was a nonintentional alloyant. The films were produced by the plasma decomposition of silane so that hydrogen incorporation results directly from the fact that not all of the H bonded to silicon is removed from the silane as the films grow.[3]

The recent trend has been to modify silicon's properties by consciously alloying it with other elements. This has resulted in the preparation of a-Si:C, a-Si:N, a-Si:Ge and a-Si:F alloys.[3,6] Most of the research to date on these materials has focused on the differences in film properties which appear with the gases containing alloyant atoms are added to the reaction mixture, these differences are usually attributed to the inclusion of the alloyant. Our research shows that attention must be paid to the actual composition and bonding of the resulting films and not just to the relative ratios of reactant gasses if the differences are to be properly explained.

** Research supported by DOE Grant #ER-78-S-02-4899 and EY-76-C-05-0033 #S-2002

+ Research sponsored by U.S. DOE Div. Basic. Energy Sci. under Contract #W-7405-Eng-26 with Union Carbide cooperation.

In the first place, unless all forms of hydrogen are rigorously excluded from the deposition zone it is likely that hydrogen as well as the desired alloyant will be incorporated into the deposit. In most processes for growing thin films containing silicon, including glow discharge and chemical vapor deposition (CVD), it is not possible to exclude hydrogen. Even if hydrogen can be excluded, in many cases it is deliberately included as an additional alloyant in an attempt to achieve the desirable electronic effects attributed to hydrogen. In the second place, it is likely that the incorporation of one element (for example, carbon) into a film may change the incorporation efficiencies of other elements (for example, H), that is, it is not justifiable to assume that the hydrogen content of a-Si:X:H is the same as that of a-Si:H prepared in the same way except for the exclusion of an alloyant gas containing element X. It is known that small amounts of hydrogen--0.25 to 0.75 at.% --are incorporated into CVD a-Si:X which confirms the importance of the first effect discussed above.[4] We have investigated the hydrogen content of CVD a-Si:C and a-Si:N to determine whether the incorporation of carbon or nitrogen changes the incorporation efficiency of hydrogen. We present evidence in this paper that it does--enhancing the incorporation efficiency of hydrogen by as much as a factor of 20.

Experimental

A total of seven samples were used in this study, one nominally non-alloyed, one a-Si:N and five a-Si:C. All were prepared by the pyrolytic decomposition of flowing gas mixtures which contain silane, helium and, if alloys were desired, any alloyant gas. The horizontal atmospheric pressure reactor was radiantly heated.

A helium carrier gas flow rate of typically 4 l/min was employed. Of the total flow, silane typically constituted 0.5 to 1.5%. The a-Si:C and the a-Si:N samples were prepared by adding gaseous acetylene (C_2H_2) and hydrazine (N_2H_4) respectively to the reaction gas mixture. The hydrazine vapor was produced by bubbling a portion of the helium carrier gas through anhydrous hydrazine held at room temperature (300K) in a stainless steel sampling cylinder. Various parameters relative to the preparation and analysis are summarized in reference 4.

The substrate temperatures during deposition for the non-alloyed a-Si, the a-Si:N and a-Si:C samples were respectively 850, 870, and 900K. The samples, which were without exception specular, were deposited on conducting substrates. The film thickness ranged from 0.4 μm for the a-Si sample to approximately 1.0 μm for the a-Si:C samples. Thickness variations were less than 5% across the area analyzed. Two samples of 35 at.%C a-Si:C deposited at the same time were employed in the study. One was subjected to a post deposition anneal for 10.2 hrs. at 1310K in a flowing 10% H_2 in N_2 atmosphere before the hydrogen was determined. The other was untreated.

The atomic fraction of all elements with atomic number (Z)> 4 included in the films was determined by electron microprobe analysis; further details can be

found elsewhere[4,9] The H content of the films was determined by the use of the 16.45 MeV resonance in the ^{1}H $(^{19}F\ \alpha\gamma)^{16}O$ nuclear reaction using the EN tandem accelerator located at Oak Ridge National Laboratory. Nuclear Reaction Analysis (NRA) is the only reliable technique for determining H in these alloys. Except for SIMS, hydrogen can not be detected by other techniques and SIMS is too susceptible to matrix effects to be used for these alloys. This particular resonance, which has a very high cross-section, good depth resolution, and can yield profiles in acceptable measurement times.[10]

The $^{19}F^{+4}$ ion beam employed was collimated by the use of two pair of adjustible tantalum slits to a spot roughly 2x2mm before striking the target. Care was taken to shield the NaI (Tl) detector from γ-rays arising from collisions of the ion beam with all H atoms except those in the surface of the target. The sample carousel had positions for 16 samples. The sample carousel sat within a copper stroud and made thermal and electronic contact. This unit, which could be cooled, was electrically isolated from the rest of the apparatus and a +300 V bias potential was applied to prevent the escape of secondary electrons from the target. The vacuum pressure was maintained at less than 10^{-6} during the measurements. The contribution of beam-tramp electrons to the integrated charge is known to be minimal (< 2%).

A hydrogen depth profile for each sample was obtained by transforming the γ-ray yield versus beam energy data using the computer program named UNFOLD which is described in reference 10. Stopping power data, necessary to convert beam energy to depth, were obtained from standard tables.[12] The calibration constant for the system, required to convert γ-ray yields to hydrogen concentration, is most accurately obtained by comparison to standards with known hydrogen content. In this experiment, particular attention was paid to obtaining the calibration constant.

Four samples, three prepared using the ion implantation facilities at the ORNL Solid State Division and one prepared at RCA, were used as calibration standards; all had been prepared by implanting silicon wafers with hydrogen. The implant doses were determined by accurate charge integration, the accuracy of which is known to be ±5%. Rastering the implant beam across the surface produces samples uniformly implanted to ±1%. The preparation procedure is discussed in Reference 13. The implant dose and the hydrogen content of the four standards are compared in Table 1. The difference between the average of the three ORNL samples and the implant from RCA is less than 10%. In addition to this agreement between the two laboratories, the consistency among the various samples implanted at ORNL is very encouraging. This confirms the utility of the technique and the reliability of the data analysis routine for small (10^{15}), as well as moderate concentrations of H and demonstrates that even at comparatively high (10^{17} H/cm^2) implant doses, H is retained in suitably prepared silicon surfaces.

Table 1

10^{15} Hydrogen Atom/cm^2

Sample	Dose*	Measured
RCA	10	10.8
ORNL 4	1	0.99 ± 0.15
ORNL 1	10	10.2 ∓ 0.3
ORNL 2	100	98.9 ∓ 1.5

* The implant dose is accurate to ± 5%

Results and Discussion

In Figure 1, the average hydrogen content H for the films studied is plotted as a function of the alloyant concentration (C or N). The hydrogen concentration for each of the samples was observed to be roughly independent of depth. The hydrogen content of the 35 at.% C film with and without anneal is also given. The [H] in non-alloyed a-Si is 0.25 at.% and rises a factor of 20 in the 35 at.% C a-Si:C alloys. the [H] of the single a-Si:N film studied is also given in the figure. An enhancement in the amount of hydrogen incorporated is also seen in the one a-Si:N sample studied. The datum point lies approximately on the curve drawn through the a-Si and the a-Si:C data, but without additional hydrogen content data for other N concentrations, we must regard the approximate coincidence as accidental. There are two distinct regions in Figure 1. Up to about 20 at.% carbon the [H] increases linearly as a function of [C] . At higher [C] the amount of hydrogen incorporated increases at a much greater rate.

The incorporation of hydrogen in CVD a-Si:X films may have passive, active or a combination of active and passive causes. A passive cause for the increased incorporation of hydrogen into a-Si:C is the greater strength of the C-H bond (99kcal/mole) relative to the Si-H bond (70kcal/mole).[13] This may account for the linear region. During the growth of a-Si:C hydrogen atoms are stripped from both carbon and silicon atoms on the film; carbon atoms will, however, have a greater probability than silicon atoms of retaining hydrogen atoms. If all other factors remain constant, increasing the number of carbon atoms in the film will proportionally increase the number of hydrogen atoms incorporated. In this scenario, the incorporation of hydrogen is happenstance; a certain fixed fraction of the carbon atoms bring hydrogen atoms with them.

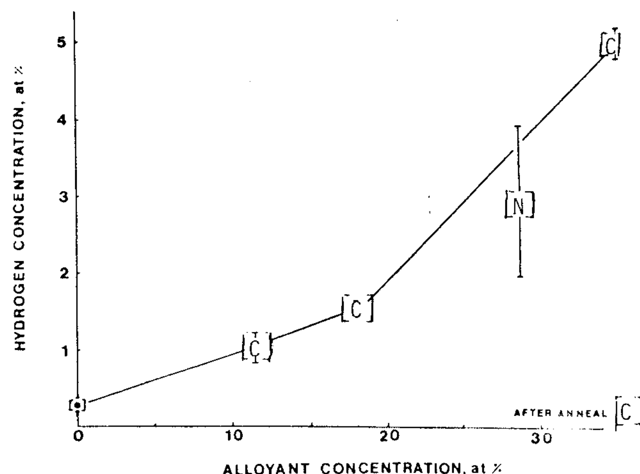

Figure 1. The hydrogen concentration [H] as a function of alloyant concentration [X] for CVD a-Si:X; [N] , nitrogen alloyed; after anneal [C] , after annealing at 1310K for 10.2 hours.

On the other hand, hydrogen may play an active role in minimizing the internal energy of high carbon a-Si:C alloys by acting as a bond terminator. The bonding radius of carbon is substantially smaller than that of silicon. Hydrogen, which has a bond order of one and has a small radius, is an ideal bond terminator for carbon and may make it possible for carbon to achieve full coordination in a-Si:C without strained bonds. The failure of any atom in CVD a-Si:C to maximize its bond order is thermodynamically unfavorable.

This comes about for the following reason: The only driving force for film growth in CVD is heat. A chemical reaction will only be appreciable if the activation energy is on the order of kT--about 0.1 eV at 1000K. Since the energy of silicon-hydrogen and alloyant hydrogen bonds is 3-4eV, in depositing CVD a-Si:X, the removal of hydrogen atoms from silane and alloyants will occur in concert with the formation of other bonds to minimize the energetic requirements of the deposition. The formation of dangling bonds via CVD is energetically too costly to occur frequently. Experimental evidence for this is the fact that the spin density of a-Si:C films is not high ($\sim 10^{19}$/cc) which implies that less than one atom in 1000 has a dangling bond.[15]

If we postulate that hydrogen plays an active role in the growth and stability of the film, it is conceivable that the hydrogen incorporation efficiency might vary as the need for bond termination varies from one alloy composition to another. However, it is impossible to predict whether deviations from linearity should be positive or negative.

It is most likely that the presence of hydrogen in a-Si:C is due to both passive and active causes. The relative difference in hydrogen bond strength for carbon and silicon accounts well for the linear increase in [H] with increasing [C] up to about 20at.% carbon. The much higher incorporation efficiency of [H] as a function of increasing [C] , beyond 20%C can be explained if hydrogen is playing an active role in the film growth. Examining the effect that the deposition conditions--particularly the deposition rate--have on [H] may aid in determining which of the causes is more important.

Booth et al.[4] have observed that during the annealing of a-Si:X alloys (X=C,N) the optical constants of the alloys shift before the onset of crystallization. Our experiments provide circumstantial evidence that the optical transformations are connected with the effusion of hydrogen from the films. The [H] content of a-Si:C with 35 at.% carbon decreases from 5%, as deposited, to nearly zero after annealing 10.2 hours at 1310K. The anneal is not sufficiently long to crystallize the a-Si:C as determined by X-ray diffraction but causes a shift in optical properties. More detailed kinetic studies will be required to determine if the loss of hydrogen coincides point by point with the optical shifts or if other factors are at work.

In addition to CVD, a-Si can be prepared by glow-discharge (or plasma assisted CVD), sputtering and evaporation. Variations in the incorporation efficiency of one alloyant because of variation in another are likely in processes such as glow-discharge[3] and reactive evaporation or sputtering where gas phase and/or surface chemical reactions are known to occur. The circumstances for which enhancement effects are important for CVD and glow-discharge a-Si alloys need to be investigated. Additionally, it is of value to determine whether other alloyants show fluctuations as pronounced as those seen for hydrogen in this study.

Attention should also be given to separating the roles of hydrogen and other alloyants in determining the alloy's optical, electronic and structural properties. In particular, it will be necessary to determine the bonding of these multicomponent alloys. The comparative strengths of carbon, nitrogen and silicon lead us to expect that the hydrogen in the films is probably bonded to carbon and nitrogen, respectively. This is by no means certain and we plan to investigate the infrared absorption of these films.

Conclusions

We have determined the [H] content of several CVD a-Si:C and a-Si:N thin films, using the 16.45 MeV resonance of the ^{1}H ($^{19}F,\alpha\gamma$)^{16}O nuclear reaction. We have found that the hydrogen concentration [H] of a-Si:C film is twenty times greater than the hydrogen composition of non-alloyed a-Si prepared in a similar fashion.

We have also found evidence that, for CVD a-Si:C for [C] $\geq$ 20 at.%, the incorporation of hydrogen into the film is not purely accidental but a necessary part of film growth; the hydrogen perhaps allows carbon to fully coordinate.

This is one of the first reports of the enhancement of one alloyant in a-Si arising from the inclusion of a second alloyant, but the effect may be common. We conclude that the common practice of denoting alloys and correlating film properties by reporting the alloyant gas ratios employed in the deposition instead of measuring film composition is suspect. Previous investigation of the optical, electronic properties of multicomponent a-Si alloys may need to be re-evaluated in light of the fact that the hydrogen content--a key parameter for determining film properties of an alloy or series of alloys--may differ significantly from one another and similarly prepared binary a-Si:H alloys and attention should be given to separating the different roles of hydrogen and other alloyants on film properties.

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