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IR absorption in glow-discharge-deposited *a*-Si:(D, O) and *a*-Si:(D, N) alloy films

G. Lucovsky,* J. Yang, S. S. Chao, J. E. Tyler, and W. Czubatyj
Energy Conversion Devices, Incorporated, Troy, Michigan 48084
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This report is a continuation of our studies of the local chemical bonding in glow-discharge-deposited (GD) ternary amorphous silicon (*a*-Si) alloys using IR-absorption spectroscopy. The spectra we obtain for high-temperature ($T_s = 300$–$400\,^\circ\mathrm{C}$) *a*-Si:(D, O) and *a*-Si:(D, N) alloys confirm the bonding models previously presented by us on the basis of studies of similar hydrogenated alloys. Studies of low-temperature films $T_s < 150\,^\circ\mathrm{C}$) support and extend the previously proposed model for *a*-Si:(H, O) films, but lead to an important modification of the bonding picture for *a*-Si:(H, N) alloys.

I. INTRODUCTION

In recent publications we discussed the IR absorption of thin films of *a*-Si:(H,O)[1] and *a*-Si:(H,N),[2] identifying differences in the local bonding arrangements of alloy atoms for films deposited via the glow-discharge-deposition (GD) technique at high (300–400 °C) and low (< 150 °C) substrate temperatures (T_s). A substrate temperature of 300–400 °C plus a low level of rf power in the GD process promotes H-atom bonding in the monohydride arrangement, while T_s below 150 °C promotes polysilane formation. Films deposited with $T_s = 400\,^\circ\mathrm{C}$ have H concentrations of approximately 10 at. %, while films deposited at 100 °C have H concentrations of about 40 at. %. Nominal O- and N-atom concentrations range from 2–8 at. %. All ternary films have H-atom concentrations in excess of the O- or N-atom concentrations and therefore display IR absorptions characteristic of Si–H bonding as well as features due to the third alloy component. This paper reports an extension of these studies in which deuterium (D) has been substituted for hydrogen (H). This substitution shifts the frequencies of all vibrations with significant H-atom motion to lower wave number, and also changes the degree of coupling for modes involving both H-atom, and O- or N-atom motions.[3] The results presented here support the bonding models presented in Ref. 1 for *a*-Si:(H, O) deposited at $T_s = 300°$ and 50 °C, and in Ref. 2 for *a*-Si:(H,N) deposited at 400 °C. They also have served to identify changes in the local bonding in low T_s *a*-Si:(H,O) and *a*-Si:(D,O) alloys that derive from changes in the starting gas mixtures, which in turn promote differences in the amount of bonded oxygen in the film. The situation is different for the *a*-Si:(H,N) films deposited at 100 °C. A shift of the polysilane scissors/wagging doublet from 890–845 cm^{-1} in the H-containing alloy[4] to 650–635 cm^{-1} in the D-containing alloy has served to clarify the nature of the IR absorptions due to Si-N vibrations, thereby leading to an important change in the structural model for these low T_s alloys.

II. *a*-Si:(D,O) ALLOYS

Figure 1 displays IR spectra for *a*-Si:(D,O) produced by the GD method using a mixture of SiD_4 and O_2 for $T_s = 400\,^\circ\mathrm{C}$. For comparison, we also include high T_s spectra for *a*-Si:H, *a*-Si:D, and *a*-Si:(H,O). Referring to the *a*-Si:(H,O) spectrum, there are four O-related features which have been interpreted using a model in which O and H atoms are bonded to the same Si atom, and in which the Si–H bond is in the plane of the Si–O–Si group.[1,3] Three of these do not depend on the particular orientation of the Si–H bond, whether it is in the cis or trans position (see Fig. 9 of Ref. 1). These are (1) *a*-Si-H stretching absorption at 2090 cm^{-1} (shifted from 2000 cm^{-1} by the second-neighbor O atom[5]); (2) an O-atom (in-plane) stretching mode at 980 cm^{-1}; and (3) an O-atom (out-of-plane) rocking mode at 500 cm^{-1}. Since the H-atom concentration is greater than the O-atom concentration, the spectrum also displays the characteristic monohydride bands at 2000 and 630 cm^{-1}. Modes involving a component of O-atom (in-plane) bending motion are qualitatively different for the cis and trans bonding arrangements.[3] For the trans conformation, the mode in question has a pure bending motion char-

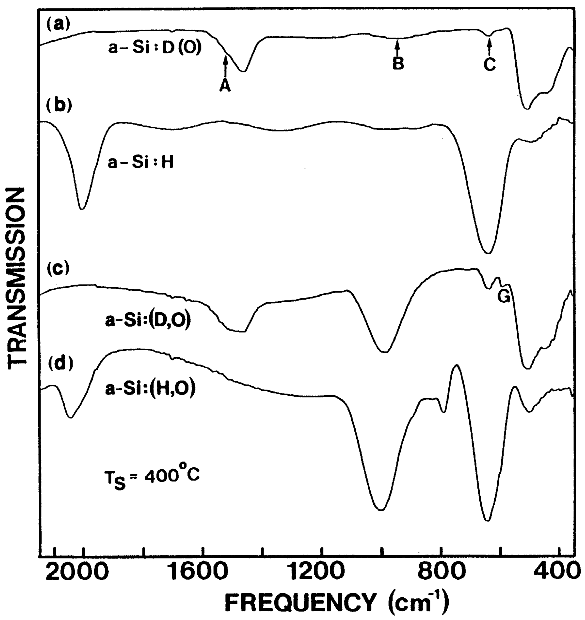

FIG. 1. IR absorption in high-T_s alloys. (a) *a*-Si:D. *A B*, and *C* indicate absorption due to O-atom contamination. (b) *a*-Si:H. (c) *a*-Si:(D,O). *G* indicates a grating change discontinuity. (d) *a*-Si:(H,O).

acter and is expected to occur at 650 cm^{-1} (Ref. 3) (this absorption is masked by the 630-cm^{-1} Si–H bending vibration); for the cis conformation there is an absorption at 780 cm^{-1} which couples a mixed bending/stretching O-atom motion with H-atom bending.[1,3] The spectra for the two deuterated alloys support the interpretation discussed above. The O-perturbed Si–H stretching vibration is shifted down in frequency by a factor equal to the square root of the D- to H- atom mass ratio, the O-atom stretching mode remains fixed at 980 cm^{-1} (it involves neither H- nor D-atom motion), and the O-rocking mode mixes with Si–D bending vibrations.[6] Finally, and most importantly, there is no feature near 780 cm^{-1}; instead there is a pure O-atom bending vibration at 650 cm^{-1}. The frequency of this mode is predicted to be indepenent of the cis or trans bonding arrangement for the D-atom substitution.[3]

Figure 2 displays spectra for films deposited with $T_s = 100\,^{\circ}\mathrm{C}$. We include two traces for alloys of *a*-Si:(H,O) to emphasize the concentration dependence of several of the features. The lower O-concentration alloy (2 at.% O), grown from a mixture of $\mathrm{SiH_4}$, $\mathrm{H_2}$, and $\mathrm{O_2}$, has O-related features at 1000, 780, and 500 cm^{-1} (the feature at 1000 cm^{-1} is masked in part by the polysilane scissors/wagging doublet). The higher concentration alloy (8 at.% O) is grown from $\mathrm{SiH_4}$ and $\mathrm{O_2}$ and shows additional features at 800, 820, 920, 1030, and 2125 cm^{-1}. We assign these to a bonding group that includes one O and two H atoms attached to the same Si atom. We show only one trace for an *a*-Si:(D,O) alloy grown from a mixture of $\mathrm{SiD_4}$ and $\mathrm{O_2}$. This alloy film (5 at.% O) displays three O-related features, all of which are in accord with the structural model discussed above. These are an O-atom stretching vibration at 1000 cm^{-1}, and O-perturbed $\mathrm{SiD_2}$ stretching vibration at 1560 cm^{-1}, and finally a mode at 720 cm^{-1} that mixes O-atom bending and D-atom wagging motions ($\mathrm{SiD_2}$ group). The spectra displayed in Fig. 2 support the assignments discussed in Ref. 1, and also reveal an additional local bonding group that becomes evident when the bonded O concentration is increased.

III. *a*-Si: (D,N) ALLOYS

Figures 3 and 4 give spectra for *a*-Si:(D,N) and *a*-Si:(H,N) deposited with $T_s = 400$ and $100\,^{\circ}\mathrm{C}$, respectively. There are three N-related features in the high T_s film: (1) a N-neighbor perturbed Si–H stretching band at 2060 cm^{-1}; (2) a Si–N (in-plane) stretching vibration at 840 cm^{-1}; and (3) a disorder-induced Si-atom breathing mode at 495 cm^{-1} which involves the three N-atom neighbors, and is made IR active via a H atom being a N-atom second neighbor (see Fig. 4 of Ref. 2). The changes in absorption upon deuteration are in accord with the bonding model given in Ref. 2. Specifically, the N-atom perturbed Si–H stretching mode is down shifted by the D- to H-atom mass ratio factor; the Si–N stretching mode, involving neither H- nor D-atom relative displacements, remains at 840 cm^{-1}; and the 495-cm^{-1} breathing mode becomes mixed with Si–D bending motions.[6] In contrast, the spectra for $T_s = 100\,^{\circ}\mathrm{C}$ deuterated films reveal new and important information relative to the local bonding arrangements of N and H (or D) atoms.

The comparison, in Ref. 2, between the IR absorption in films of *a*-Si:(H,N) and *a*-Si:H lead to the identification of three N-related features: (1) a Si–N stretching vibration at 790 cm^{-1}, and (2) two features related to the presence of H–N bonding groups—a stretching mode at 3350 cm^{-1}, and a bending mode at 1150 cm^{-1}. [Note that films of *a*-Si:(H,O) with comparable ratios of O to H atoms never

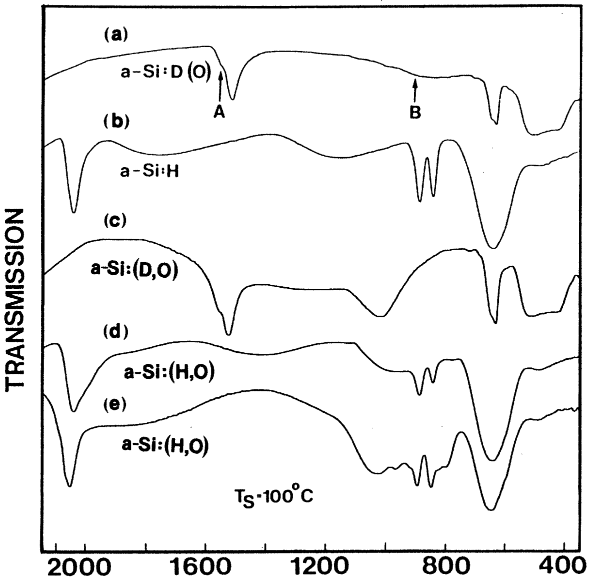

FIG. 2. IR absorption in low-T_s alloys. (a) *a*-Si:D. *A* and *B* indicate absorption due to O-atom contamination. (b) *a*-Si:H. (c) *a*-Si:(D,O) (prepared from $\mathrm{SiD_4}$ and $\mathrm{O_2}$). (d) *a*-Si:(H,O) (prepared from $\mathrm{SiH_4}$, $\mathrm{H_2}$, and $\mathrm{O_2}$). (e) *a*-Si:(H,0) (prepared from $\mathrm{SiH_4}$ and $\mathrm{O_2}$).

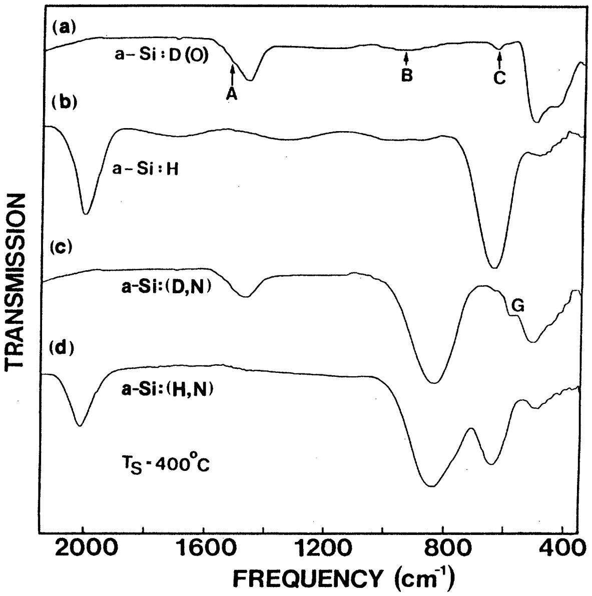

FIG. 3. IR absorption in high-T_s alloys. (a) *a*-Si:D. *A*, *B*, and *C* indicate absorption due to O-atom contamination. (b) *a*-Si:H. (c) *a*-Si:(D,N). *G* indicates a grating change discontinuity. (d) *a*-Si:(H,N).

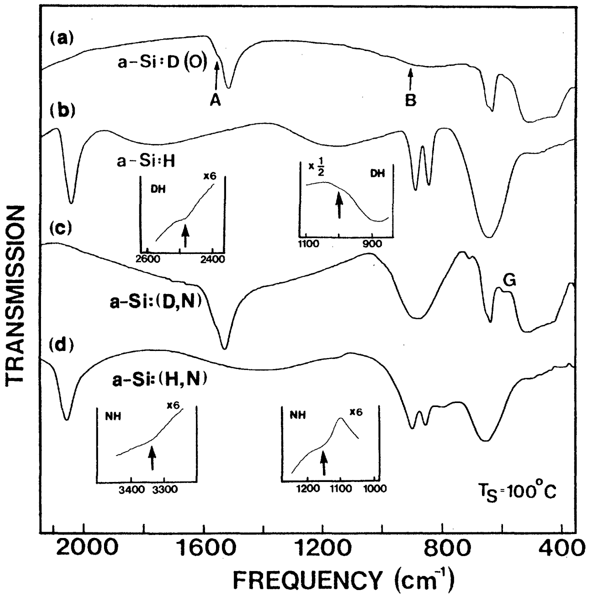

FIG. 4. IR absorption in low-T_s alloys. (a) *a*-Si:D. *A* and *B* indicate absorption due to O-atom contamination. (b) *a*-Si:H. (c) *a*-Si:(D,N). *G* indicates a grating change discontinuity. The inserts indicate the position of the D-H internal vibrations. (d) *a*-Si:(H,N). The inserts indicate the positions of the H–N internal vibrations.

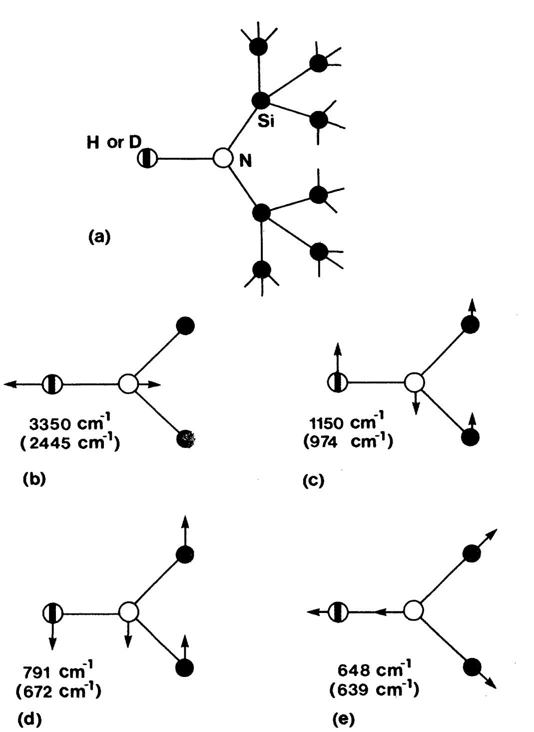

FIG. 5. (a) Local bonding at H–N (or D–N) site. Alloy atom local mode atomic displacements. Internal modes of H–N (and D–N) group: (b) bond stretching and (c) bond bending. The frequencies in parentheses are for the D–N group and those outside for the H–N group. External modes: (d) shearing and (e) stretching.

display absorptions characteristic of O–H bonding groups.[1,3]] The frequency of the Si–N stretching mode, as well as no additional N-related absorption near 495 cm^{-1} prompted us to assign the 790-cm^{-1} absorption to an "isolated" N-atom bonding group in which the three Si neighbors were not bonded to other N atoms, or to H atoms. The remaining absorption in this film is due to polysilane bonding arrangements.[4] The studies of deuterated alloys discussed below have lead to a modification of the model for N-atom incorporation. The IR spectrum of the *a*-Si:(D,N) alloy ($T_s = 100\,^\circ\mathrm{C}$) shows four N-atom related features, a strong band centered at 875 cm^{-1}, weaker features at 2480 and 705 cm^{-1}, and, finally, a shoulder (on the 875-cm^{-1} band) at about 980 cm^{-1}. On the basis of respective scaling factors of 1.37 (3350/2480) and 1.18 (1150/980), the two vibrations at 2480 and 980 cm^{-1} are assigned to stretching and bending vibrations of a D–N group. The absorption at 875 cm^{-1} has the same frequency as the Si–N vibration in *a*-Si_3N_4,[7] suggesting that it is derived from regions of the alloy that have the same local bonding as *a*-Si_3N_4. The assignment of the feature at 705 cm^{-1} requires a further consideration of the local bonding arrangement associated with the D–N and H–N absorptions.

Figure 5 indicates a model for the local bonding in the vicinity of the H–N and D–N groups. We have terminated the remaining two bonds on the N atom with Si neighbors (assuming a planar geometry) and have connected these to an additional shell of Si atoms.[8] This gives a ten-atom cluster, which is of sufficient intermediate size for a calculation of the character of alloy atom local vibrations.[8,9] We adjust the H–N two- and three-body near-neighbor forces (VFF representation[9]) to give frequencies of 3350 and 1150 cm^{-1} for the respective H–N stretching and bending vibrations. We employ Si-N and Si-Si forces that are essentially the same as those used in the model calculations of Ref. 2 and have calculated the complete set of local mode alloy atom vibrations which we display in Figs. 5(b)–5(e). The two high-frequency vibrations are the H–N stretching [Fig. 5(b)] and bending [Fig. 5(c)] modes, and the remaining two vibrations involve relative displacements of the H–N group and the neighboring Si atoms and are at frequencies of 791 and 648 cm^{-1}. Also included in the figure are the frequencies of the same modes for D-atom substitutions. The internal vibrations of the D–N group are at 2445 and 974 cm^{-1}, and the other two vibrations are at 672 and 639 cm^{-1}. Based on this model calculation we assign the 790-cm^{-1} absorption in *a*-Si:(H,N) and the 705-cm^{-1} absorption in *a*-Si:(D,N) to "external" vibrations of the N–H or N–D groups, respectively, as shown in Fig. 5(d). The vibration displayed in Fig. 5(e) is assumed to be masked by the 630-cm^{-1} Si–H bending absorption in *a*-Si:(H,N) and the 650/635–cm^{-1} doublet in the *a*-Si:(D,N) film. We have also calculated the vibrational properties for a bonding configuration that is pyramidal and find modes qualitatively similar to those discussed above. These calculations have therefore established the origin of the 705- and 790-cm^{-1} absorptions, but they do not identify all the details of the local bonding configuration, e.g., the planar geometry.

The assignments given above have led to a reexamination of the *a*-Si:(H,N) spectrum of Fig. 4, and have led us to conclude that a Si–N band is present in that film near 875 cm^{-1} but is in part obscured by the 890–845-cm^{-1} polysilane doublet. Since the *a*-Si:(H,N) alloy is known to be inhomogeneous with a columnar structure,[2] we did not attempt a deconvolution which might reveal the obscured band. The assignments discussed above have lead to the following modification of the model proposed in Ref. 2. We view the low-T_s a-Si:(H,N) and a-Si:(D,N) alloys as being inhomogenious with two phases dominating: (1) a polysilane connective tissue phase; and (2) an a-Si:N phase in which the N atoms are clustered and occur in regions with the local bonding of a-Si_3N_4. This last point is supported by x-ray photoemission spectroscopy measurements which reveal a high-energy satellite of the Si 2p line. Finally, we assume that the H–N and D–N groups are located in the neighborhood of the boundary between the two phases.

IV. SUMMARY

We have reported IR measurements of the a-Si:(D,O) and a-Si:(D,N) alloys which serve to complement measurements reported previously for similar H-containing alloys. The analysis of the new data reported here confirms the assignments made for the high-T_s films where monohydride bonding dominates, and O- and N-atoms have second-neighbor H or D atoms. The low-T_s studies have revealed concentration-dependent aspects of O bonding in the a-Si:(H,O) and a-Si:(D,O) alloys as well as an additional feature in the N ternary alloys. This has lead to a modification of the bonding model for the N alloys.

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[*] Permanent address: Department of Physics, North Carolina State University, Raleigh, NC 27650.

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