Dopant-atom-induced disorder in hydrogenated amorphous silicon: Raman studies

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(Received 25 March 1988; revised manuscript received 13 March 1989)

Raman scattering measurements on thin films of undoped and B- and P-doped hydrogenated amorphous silicon (*a*-Si:H) alloys have been reported. The doped samples indicate considerable concentration-dependent changes in the longitudinal vibrations as well as in the position and full width at half-maximum of the optical band relative to the undoped samples. These dopant-atom-induced changes in Raman spectra are attributed to the modification of hydrogen microstructure and consequently to the degraded short-range order. These changes are proposed to degrade the doping efficiency in *a*-Si:H alloys.

I. INTRODUCTION

To what extent the structural order in the purely amorphous phase can be modified and the degree to which such order influences the optoelectronic properties of amorphous alloys, particularly hydrogenated amorphous silicon (*a*-Si:H), have been topics of current interest. By now, it is well established that H in *a*-Si:H alloys not only neutralizes the dangling-bond defects near the Fermi level and improves the dopability of the amorphous Si-atomic network,[1] but also improves the degree of short-range order (SRO) in the bulk of the material.[2,3] The improved SRO in the unhydrogenated amorphous silicon (*a*-Si) and *a*-Si:H alloys has been observed to play an important role in controlling the band gap[3,4] as well as in lowering the defect density of states.[5] These SRO effects have been successfully correlated to the "intrinsic" changes in the network structure.

The doped *a*-Si:H, however, additionally involves the "extrinsic" effects, such as the micromorphological changes associated with the dopant-atom configurations. Hence, it would be of considerable interest and importance to understand how the dopant atoms affect the SRO and in turn how the SRO affects the doping processes in *a*-Si:H alloys.[6,7] We have, therefore, for the first time, presented here the Raman scattering (RS) studies on B-doped [(*a*-Si:H):B] and P-doped [(*a*-Si:H):P] alloy films having thicknesses (500 Å) equal to those of doped layers in solar cells, but deposited on optically polished stainless-steel (SS) substrates. This special choice allows an enhancement of the Raman signal[8] by at least a factor of 2, compared to that observed for the thicker films deposited on other substrates. We discover here a strong evidence for the dopant-atom-concentration-dependent degradation of SRO in *a*-Si:H alloys.

II. EXPERIMENTAL

a-Si:H films were deposited by a conventional rf plasma-assisted chemical vapor deposition (RF-PA-CVD) reactor obtained from Messers Annelva, Japan. The *a*-Si:H films were deposited by using pure silane, whereas mixtures of pure silane and 1 vol % B_2H_6 and 1 vol % of PH_3 in silane, respectively, were used to produce *a*-(Si:H):B and *a*-(Si:H):P films with different dopant concentrations. The doping level is measured in terms of the dopant-gas-volume concentration in the plasma. To obtain films of varying thicknesses only the time of deposition was varied. Other deposition parameters were kept unchanged, e.g., $T_s \sim 260\,°C$, rf power density ~ 0.06 W/cm^2, pressure ~ 0.5 Torr, deposition rate ~ 2 Å/sec^{-1}, and gas-flow rate ~ 10 (cm^3/min at STP).

Raman measurements in the photon-counting mode were performed using a SPEX 1403 double spectrometer with the SPEX 1442 third monochromator, a C31034 GaAs-photomultiplier detector (PMT) system, and a SPEX DM1 DATAMATE spectrometer controller and data processor. The filtered radiation of 514.5 nm from an argon-ion laser formed the excitation source (for details see Ref. 8). The spectra were scanned in the region 10–1210 cm^{-1} with steps of 2 cm^{-1} and an integration time of 20 sec. The data were plotted after a light smoothing by using the built-in software of the DM1 and subtracting the PMT dark counts [~ 10 (photon counts)/sec]. The background reference line used for half-width calculations equals the photon counts at 1200 cm^{-1} and is indicated by the zero line on the right-hand side for each Raman curve.

III. RESULTS AND DISCUSSION

The Stokes scattering amplitude (I_w) in the first-order Raman spectrum of intrinsic fundamental vibrations of the amorphous Si network is related to the vibrational density of states (VDOS), g_w, through the approximate relation[9]

$$I_w \sim C_w[(n+1)/w]g_w \cdots , \quad (1)$$

where C_w is assumed to be a smoothly varying electron-phonon coupling constant and n is the Bose-Einstein fac-

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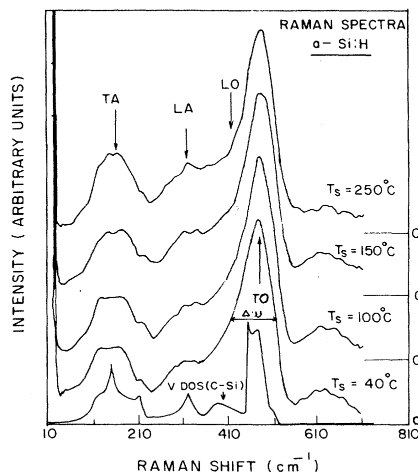

FIG. 1. Raman spectra of undoped *a*-Si:H alloy films deposited at different substrate temperatures (T_s) are compared.

tor. Since the tetrahedral bonding (sp^3) is retained in the amorphous Si network, g_w becomes simply a broadened version of crystalline VDOS (ρ_w) (Ref. 10) shown in Fig. 1. The Raman spectra of our amorphous materials are therefore described in terms of different distinct spectral regions of intrinsic vibrations in *c*-Si, e.g., the transverse-acoustic (TA) band, the longitudinal-acoustic (LA) and longitudinal-optical (LO) bands, and the transverse-optical (TO) band. Further, the C_w effects[10] change less significantly and therefore the I_w can be taken as an approximate experimental measure of g_w. Theoretically, g_w is understood to be a good sensitive function of SRO defined in terms of the deviations from tetrahedral symmetry, bond-angle distortion ($\Delta\theta$), and ratio of the odd to even-membered rings.[11] A variety of model calculations[12] on g_w have shown that the width (Γ) of the TO band can be directly related to the $\Delta\theta$, and is, therefore, considered an important parameter for measuring the SRO in various films in the present study. In the frame of reference just summarized, we describe our results as follows.

A. Raman measurements on undoped *A*-Si:H films

These films were deposited at T_s of 40, 100, 150, and 250 °C, and many more temperatures ranging up to 390 °C. Thick samples deposited on *c*-Si substrates, particularly at T_s=40 and 250 °C, indicated Si—H stretching-mode infrared absorption near 2090 and 2000 cm^{-1}, respectively. Similar results have been well established in the literature,[13] and therefore we reasonably assume that the H concentration diminishes in our *a*-Si:H films with the increase in T_s, whereas the H microstructure (HMS) changes from dihydrogenlike clusters (—SiH_2) at T_s=40° C to the monohydrogenlike clusters (—SiH) at T_s=250 °C.

The Raman spectra of thin samples are compared in Fig. 1 with the ρ_w VDOS for *c*-Si. The TO band in the Raman spectrum of the 40 °C sample displays large asymmetry from the LO region, and shape similar to that of the Raman spectrum of polysilanes.[14] This observation indicates the presence of $(\text{—SiH}_2)_n$-like portions in the bulk of the 40 °C film. Next, as the T_s changes from 40 to 250 °C, the spread of the TO band diminishes and the LA band develops a sharper feature, which increases in intensity, while the LO band diminishes in intensity, leaving a dip in the LA-LO region. This dip appears to be deeper for films deposited at $T_s \sim 250$ °C than for those deposited at either $T_s < 250$ °C or $T_s > 250$ °C. The Raman spectra of *a*-Si:H films deposited at $T_s > 300$ °C have displayed a TO-band position at 480 °C with a slight definite increase in TO-band width, and LO intensity similar to those of chemical-vapor-deposits (CVD) materials[2] deposited at T_s=625 °C. The TO-band position and width decrease continuously with the increase in T_s, and saturate to values of 480 and 84 cm^{-1} [Fig. 4(a)], respectively.

The dip in the LA-LO region of the Raman spectrum of the films deposited at $T_s \sim 250$ °C can be compared with the dip in the LA-LO region of the well-established curve for the VDOS for *c*-Si. The LA-LO bands in the VDOS for *c*-Si are known to originate from the six-membered closed rings of Si atoms in the diamondlike crystal structure, and therefore represent long-range order (LRO) in *c*-Si. Such ring-structure analysis of g_w for *a*-Si or *a*-Si:H is not yet known to a reliable level. However, the similarity of dips may be inferred qualitatively to reflect a high quality of SRO in *a*-Si:H films deposited at T_s=250 °C. Alternatively, we regard the $T_s \sim 250$ °C as a good parameter for deposition of doped *a*-Si:H films for evaluation of the effect of dopant atoms on SRO in *a*-Si:H.

B. Raman measurements on doped *a*-Si:H

Raman spectra of *a*-(Si:H):B (Fig. 2) and *a*-(Si:H):P (Fig. 3) samples are compared with that of undoped *a*-Si:H films. All doped samples were deposited at T_s=260 °C, and their thicknesses were restricted to $\sim 450 \pm 50$ Å. The following changes have been observed while comparing the Raman spectra of *a*-Si:H with those of doped samples.

(1) Since we have prepared all three kinds of films under identical conditions of deposition, particularly the same T_s, these samples were expected to have approximately the same HMS and H concentration and, therefore, also the same TO-band position.[15] In contrast, we observe a continuous shift in TO-band position from 480 to 472 cm^{-1} as a function of the increase in dopant-gas concentration from 0.0 vol % to 1.00 vol % [Figs. 4(b) and 4(c)].

(2) The TO-band width (Δw) at half maximum increases from 84 to 100 cm^{-1} as a function of dopant concentration [Figs. 4(b) and 4(c)].

(3) With an increase in dopant concentration, the LA band near 300 cm^{-1} drops in intensity and loses sharpness, while the LO band near 380–400 cm^{-1} acquires more strength. These features appear similar to those observed in the Raman spectra of the rf sputter-deposited *a*-Si films.[2]

(4) The broad band near 635 cm^{-1} gains intensity and shifts to 610 cm^{-1} for *a*-(Si:H):B, whereas it splits into

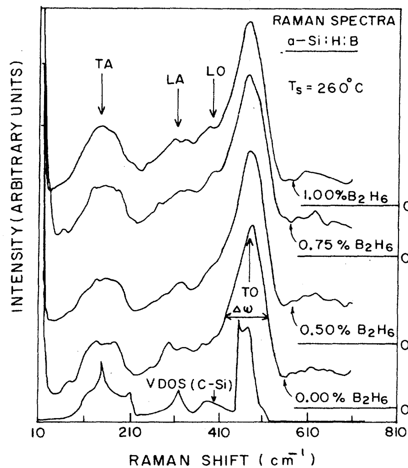

FIG. 2. Raman spectra of B-doped a-Si:H samples (labeled with gas-phase concentration of B_2H_6 in silane) are compared with that of undoped a-Si:H. VDOS curve corresponds to vibrational density of states for the crystalline Si.

two bands centered at 610 and 650 cm^{-1} in the a-(Si:H):P.

The most appropriate approach for understanding such results would be to compare the measured Raman spectra with the theoretically predicted spectrum of g_w as a function of various combinations of elements of SRO and LRO (Ref. 11) for a variety of structural models. At present, however, such detailed calculations, which could take into account simultaneously all the elements of SRO and LRO, have not yet been reported. Nevertheless, the calculations on changes in g_w involving only individual elements of disorder are available and we believe that these can provide us with a guideline for appreciating the present Raman results on the disorder effects of dopant atoms. For example, the calculations of g_w using a simple Bethe-lattice model have confirmed that the TA- and TO-like bands originate mainly from the tetrahedral SRO.[16] Studies on the effect of bond-angle distortion on these bands have revealed that the TO-band width increases with the increase in the $\Delta\theta$ and that the $\Delta\theta$ fluctuations do not produce features in the LA-LO region.[17–20] It appears that the LA-LO features probably originate more likely from the ordering effects beyond SRO, particularly the ring structure. The specific effects of topological disorder have been treated separately by several theoreticians.[16,20] They demonstrate conclusively that the structure in the LA-LO region is due to the presence of closed rings of bonds in the network of the structure of the amorphous solid. If only sixfold rings were present, the LA and LO peak features resolve considerably, as is evident in the VDOS ρ_w for c-Si, whereas if proportions of sixfold rings were decreased by the introduction of proportionate fivefold rings, the single feature near the LO band becomes prominent.[20] Thus, the surprisingly high similarities in the VDOS (c-Si) and the Raman spectra (Fig. 1), particularly in the LA-LO region, suggest that the bulk of the undoped a-Si:H film ($T_s = 250\,^{\circ}C$) may be dominated by sixfold rings of bonds.

On the other hand, the large variations of the TO-band width (Δw) and TO-band position [Figs. 4(b) and 4(c)] in the doped material can be correlated to the increase in bond-angle fluctuations, whereas the filling up of the dip in the LA-LO region can be attributed to changes in g_w probably due to the decrease in the six-membered rings in the bulk of the doped a-Si:H. Figures 4 and 5 indicate that the disorder ($\Delta\omega$ or $\Delta\theta$) in the doped samples increases continuously with the increase in dopant concentration.

Given the extremely small concentration of dopants ($<1\%$) compared to the hydrogen concentration ($>10\%$) of undoped films, the large changes in Δw and the ring statistics would be difficult to understand on the basis of variable bonding configurations of dopant atoms

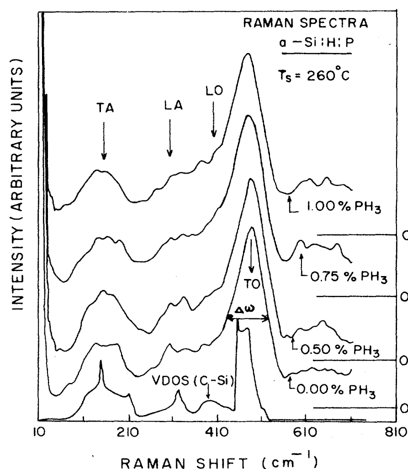

FIG. 3. Raman spectra of P-doped a-Si:H samples are compared with that of undoped a-Si:H.

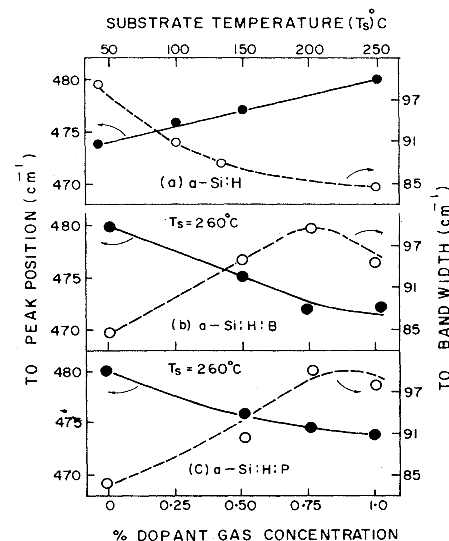

FIG. 4. Variations of TO-band width (open circles) and TO peak position (solid circles) (a) as a function of T_s for pure a-Si:H alloys, (b) as a function of B_2H_6 concentration, and (c) as a function of PH_3 concentration.

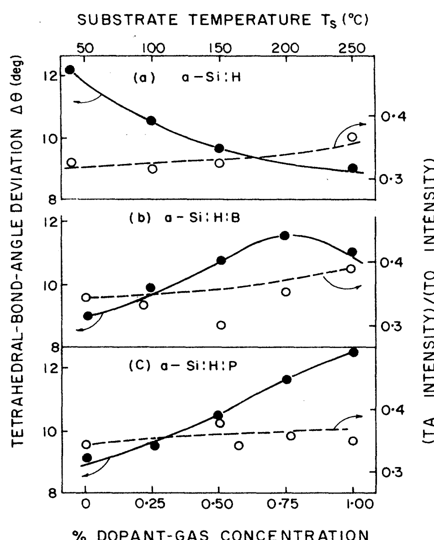

FIG. 5. Variation of tetrahedral bond-angle deviation [$\Delta\theta$ (deg)] (solid circles) and ratio of TA band intensity to the TO band intensity (open circles) (a) as a function of T_s for pure *a*-Si:H alloys, (b) as a function of B_2H_6 concentration, and (c) as a function of PH_3 concentration.

alone. Recently, Gleason *et al.*[21] observed that the dopant atoms, like B or P, affect the HMS considerably, with P causing the large H clusters to form B reducing H clustering in the film, while the total H content in both kinds of doped samples was found to decrease. The comparison of the Raman spectra of doped materials with those of unhydrogenated *a*-Si samples prepared by the rf sputter-deposition technique[2] and of the highly hydrogenated[3] RF-PA-CVD pure *a*-Si:H samples indicates that doped materials would have disorder introduced also due to the reduction in H concentration and altered HMS.

Thus we find that the dopant-atom-induced disorder is linearly dependent on the dopant concentration. On the other hand, the doping efficiency has been observed to be inversely proportional to the dopant concentration.[6,7] The present results, therefore, suggest that the degree of SRO can be another factor which needs to be considered while investigating doping processes in *a*-Si:H. For instance, the extremely low values of $\Delta\theta$ ($\sim 7.5\,^{\circ}\mathrm{C}$) and the similarity of dip in LA-LO vibrations in the undoped *a*-Si:H to that of the VDOS (*c*-Si) may be considered as a basis for speculating upon the presence of ordering effects beyond SRO that may lead to the generation of small regions of atomic configurations which have topological constraints similar to those of the crystalline state and may be surrounded by highly disordered tissuelike regions. When a dopant atom gets incorporated in the midst of a former atomic configuration, it would favor fourfold coordination, giving rise to an effective doping state, with a stress developed on the surrounding atomic network producing bond-angle disorder. An increase in the dopant concentration would increase the disorder and consequently increase the concentration of other regions of disordered atomic configuration, which would allow the dopant atoms to satisfy their natural valence permitted by the $8-N$ rule.[22] In such a situation, the doping efficiency would be greater at the lower impurity concentration, whereas it would degrade with the increasing dopant concentration.

ACKNOWLEDGMENTS

The authors acknowledge partial support for this research work from the Department of Science and Technology, Government of India, New Delhi, under the Indo-U.S. Science and Technology Initiative program. This work is a communication (No. 4410) from National Chemical Laboratory, Pune.

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