Evidence for coupling of Si–Si lattice vibration and Si–D wagging vibration in deuterated amorphous silicon

An Shih and Si-Chen Lee

Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

Chih-ta Chia

Department of Physics, National Normal University, Taipei, Taiwan, Republic of China

(Received 14 January 1999; accepted for publication 2 April 1999)

The Raman spectra of hydrogenated and deuterated amorphous silicon films (*a*-Si:H, *a*-Si:D) have been investigated. It is suggested that the asymmetrical broadening of the transverse-optical (TO) Raman peak of *a*-Si:D compared to the TO Raman peak of *a*-Si:H results from the coupling between the Si–D wagging mode and the Si–Si TO phonon mode rather than the structural difference. © 1999 American Institute of Physics. [S0003-6951(99)02922-8]

The use of hydrogenated amorphous silicon (*a*-Si:H) has been seriously limited by light-induced degradation of the photoconductivity, a phenomenon generally regarded as the Staebler–Wronski effect (SWE). Recently, hot-electron degradation in silicon metal–oxide–semiconductor field-effect transistors (MOSFET) has been found to be greatly reduced by passivating the silicon–silicon dioxide interface using deuterium instead of hydrogen.¹ And several reports^{2–7} also show that the incorporation of deuterium instead of hydrogen in amorphous silicon (*a*-Si:D) tends to slow the decay of its photoconductivity under illumination. Besides, Sugiyama, Yang, and Guha⁸ have demonstrated that an *a*-Si:D solar cell is more stable than an *a*-Si:H solar cell in normal operation. Van de Walle and Jackson⁷ and Wei, Sun, and Lee⁹ both suggested that the improvement of degradation resulted from the coupling of the Si–Si lattice transverse-optical (TO) mode and the Si–D wagging mode, because the Si–D wagging mode is very close to the Si–Si TO mode, and the accumulated energy of Si–D sites can be

easily released. As a result, the probability of breaking the nearby weak Si–Si bonds is significantly reduced. In this letter, the broadening of the Si–Si TO mode resulting from the coupling is characterized in detail by Raman spectra.

Both *a*-Si:H and *a*-Si:D films are prepared by two different methods. In the first method, undoped *a*-Si:H (*a*-Si:D) films were deposited on 7059 glass by plasma-enhanced chemical-vapor deposition (PECVD), making use of the SiH₄+H₂ (SiD₄+D₂) mixture. The deposition parameters are as follows: 0.11 W/cm² rf power density, 250 °C substrate temperature, 0.4 Torr chamber pressure, 5 sccm SiH₄ (SiD₄) flow rate, and 2 sccm H₂ (D₂) flow rate. The growth rates of *a*-Si:H and *a*-Si:D are 0.3 and 0.45 nm/s, respectively. The *a*-Si:H (*a*-Si:D) films deposited by PECVD are, typically, 100 nm or 1 μm thick. In the second method, the 100 nm *a*-Si:H films deposited by PECVD were annealed at 550 °C for 5 min in N₂ ambient environment to expel all the hydrogen atoms from the films. Then, the annealed films were treated separately by H₂ and D₂ plasma to

FIG. 1. (a) Raman spectra of 1 μm thick as-deposited *a*-Si:H and *a*-Si:D thin films. The solid line represents the spectrum of *a*-Si:D and the dashed line represents the spectrum of *a*-Si:H. (b) Enlarged view of the TO phonon mode in (a).

TABLE I. The peak position and FWHM of the Raman TO spectra, and hydrogen or deuterium concentration of *a*-Si:H, *a*-Si:D, annealed *a*-Si, and *a*-Si, treated by hydrogen or deuterium plasma.

Thin film	TO peak (cm ⁻¹)	FWHM (cm ⁻¹)	H or D concentration (%)
As-deposited 1 μ m <i>a</i> -Si:H	478.2	57.7	14.3
As-deposited 1 μ m <i>a</i> -Si:D	480.8	64.5	17.3
Annealed 100 nm <i>a</i> -Si	472.4	64	
<i>a</i> -Si treated by hydrogen plasma	472.3	64	16.5
<i>a</i> -Si treated by deuterium plasma	476.6	74	17.8

passivate the dangling bonds until their electrical properties (dark and photoconductivities) were recovered. The plasma treatment conditions are as follows: 250 °C substrate temperature, 6 Torr chamber pressure, 3 sccm H₂ (D₂) gas flow rate, and 0.11 W/cm² power density. The initial dark conductivities (σ_{D0}) and 1AM1 (100 mW/cm⁻¹) photoconductivities (σ_{L0}) of those films are 2.2×10^{-9} and 1.9×10^{-4} (Ω cm)⁻¹ for as-deposited *a*-Si:H, 1.5×10^{-9} and 1.1×10^{-4} (Ω cm)⁻¹ for as-deposited *a*-Si:D, 1.7×10^{-8} and 3.7×10^{-4} (Ω cm)⁻¹ for plasma-treated *a*-Si:H, and 1.4×10^{-9} and 4.0×10^{-4} (Ω cm)⁻¹ for plasma-treated *a*-Si:D. The hydrogen and deuterium concentration of these samples, which are calculated by secondary-ion-mass spectrometry (SIMS) and infrared spectroscopy are listed in Table I. The ratio of the Si-H stretching mode peak at 2000 cm⁻¹ to the peak at 2080 cm⁻¹ is 1 to 0.13 in as-deposited *a*-Si:H, and the ratio of the Si-D stretching mode peak at 1456 cm⁻¹ to the peak at 1506 cm⁻¹ is 1 to 1.1 in as-deposited *a*-Si:D. The Si-H stretching mode of the sample treated by hydrogen plasma is almost entirely at 2000 cm⁻¹, and the Si-D stretching mode of the sample treated by deuterium plasma is mostly at 1456 cm⁻¹. The Raman signal was measured by a DIOR XY800 triple-grating Raman spectrometer. The Raman spectra of the samples were measured at room temperature in vacuum using an Ar laser with a 514.5 nm wavelength.

Figure 1(a) displays the Raman spectra of *a*-Si:H and

FIG. 2. Raman spectra of 100 nm thick as-deposited *a*-Si:H and *a*-Si, which have been annealed at 550 °C for 5 min and all hydrogen atoms have been driven out of the film. The solid line represents the spectrum of as-deposited *a*-Si:H and the dashed line represents the spectrum of the annealed *a*-Si.

a-Si:D films which are 1 μ m thick. Several peaks are found in both *a*-Si:H and *a*-Si:D Raman spectra. For example, a main peak located at 478 cm⁻¹ corresponds to the TO phonon of *a*-Si,¹⁰ a peak at 314 cm⁻¹ corresponds to the longitudinal-acoustical (LA) phonon,¹⁰ and a peak at 140 cm⁻¹ corresponds to the transverse-acoustical (TA) phonon.¹⁰ In addition to the above three peaks, a shoulder at 390 cm⁻¹ is observed, and it corresponds to the LO phonon.¹⁰ Moreover, a small peak at 620 cm⁻¹ is also observed. It is attributed to the local wagging mode of the Si-H bonds suggested by Brodsky *et al.*,¹¹ and may also be the overtone of the Si LA phonon proposed by Cardona and

FIG. 3. (a) Raman spectra of 100 nm thick samples treated by hydrogen or deuterium plasma. The solid line represents the spectrum of *a*-Si treated by deuterium plasma and the dashed line represents the spectrum of *a*-Si treated by hydrogen plasma. (b) Enlarged view of the TO phonon mode in (a).

Bermejo.¹² It is interesting that the peak at 620 cm^{-1} of $a\text{-Si:H}$ is larger and broader than that of $a\text{-Si:D}$, which does not have the Si-H wagging mode. Therefore, the peak at 620 cm^{-1} of the $a\text{-Si:H}$ film is a mixture of the 2 LA Si-Si phonon mode and the Si-H wagging mode. Figure 1(b) displays the enlarged view of the TO phonon peaks of $a\text{-Si:H}$ and $a\text{-Si:D}$, and apparently, the difference is not symmetrical. This suggests the reason for the larger full width at half maximum (FWHM) of the $a\text{-Si:D}$ film is not that the $a\text{-Si:D}$ film is more disordered, but originates from the coupling of the Si-D wagging mode and Si TO lattice vibration. Table I lists the FWHM of the TO phonon mode and the positions of the TO Raman peaks of all the films. The FWHM of the as-deposited $a\text{-Si:D}$ film (64.5 cm^{-1}) is larger than that of $a\text{-Si:H}$ (57.7 cm^{-1}) by 6.8 cm^{-1} and the TO position of $a\text{-Si:D}$ is a little higher than that of $a\text{-Si:H}$.

In order to make sure whether the difference of Fig. 1(b) results from the structural difference of the two films, the plasma treatment is used to prepare the $a\text{-Si:H}$ and $a\text{-Si:D}$ films. Figure 2 shows the Raman spectrum of $a\text{-Si}$, which is annealed at 550°C for 5 min. The FWHM of the annealed $a\text{-Si}$ is larger than that of the as-deposited $a\text{-Si:H}$. It is because H atoms might increase the structural order and reduce the network strains. Therefore, $a\text{-Si}$ is more disordered than $a\text{-Si:H}$.¹³ Figure 3 indicates the Raman spectra of the plasma-treated $a\text{-Si:H}$ and $a\text{-Si:D}$. As listed in Table I, the TO peak of $a\text{-Si}$ treated by deuterium plasma also slightly shifts to higher energy, and the FWHM of the TO phonon mode of the deuterium plasma treatment, 74 cm^{-1} , is wider than that of the hydrogen-treated $a\text{-Si:H}$, 64 cm^{-1} , by 10 cm^{-1} . The hydrogenation of $a\text{-Si}$ does not change the FWHM of its Raman peak, i.e., both are 64 cm^{-1} , thus it does not change the disorderedness of the network. It is expected that the deuteration of $a\text{-Si}$ will not increase its dis-

orderedness, either. Therefore, the broadening TO peak FWHM of the sample treated by deuterium plasma to 74 cm^{-1} comes from the coupling of the Si-D wagging mode and the Si-Si TO phonon rather than the structural difference.

We come to the conclusion that the difference of the TO phonon peaks between $a\text{-Si:H}$ and $a\text{-Si:D}$ is asymmetrical, and is caused by the overlap of the Si TO phonon and the Si-D mode. This result further supports that the improvement of the material degradation of $a\text{-Si}$ results from the coupling of Si-Si lattice transverse-optical mode and the Si-D wagging mode.

This work is supported by the National Science Council of the Republic of China under Contract No. NSC88-2215-E-002-008.

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