

Raman study of ultrathin films of hydrogenated amorphous silicon

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We have measured Raman spectra of ultrathin films of hydrogenated amorphous silicon having thicknesses down to 1.5 nm. The TO modes of the ultrathin films are slightly different from those of bulk amorphous silicon. The microscopic morphological changes during the initial stages of growth have been discussed.

Raman-scattering studies of amorphous materials give us information about the structure, bonding, and disorder. Hydrogenated amorphous silicon (*a*-Si:H) has been extensively studied by Raman spectroscopy to obtain information about the short-range order.¹ The first-order Raman spectra of *a*-Si consist of features associated with the crystalline phase but broadened by disorder.² In plasma-deposited *a*-Si:H, the most intense mode (TO) shifts from ~ 470 to ~ 480 cm^{-1} as substrate temperature increases from ~ 160 to 330°C .³ This is similar to the trend observed in sputtered *a*-Si:H and is correlated with improved short-range order.⁴ In sputtered *a*-Si:H, the TO band shifts towards higher frequencies (~ 480 cm^{-1}) and its width decreases to ~ 80 cm^{-1} with increasing hydrogen incorporation;^{5,6} however, in glow-discharge-deposited material, the hydrogen content does not affect the TO bandwidth (~ 70 cm^{-1}) or position.³ The application of high pressure has also been found to lead to narrowing of the TO band in sputtered *a*-Si:H down to ~ 60 cm^{-1} , as well as to shifting to higher frequencies (~ 500 cm^{-1}).⁶ The shift towards higher frequencies and narrowing of the TO band is consistent with improved short-range order¹ towards the crystalline structure, which exhibits a TO band of width ~ 30 cm^{-1} at ~ 520 cm^{-1} .

The initial stages of growth of *a*-Si:H have been studied using real-time infrared reflection-absorption spectroscopy⁷ and infrared ellipsometry.⁸ Spectroscopic ellipsometry has shown that the void density and surface morphology change during growth.^{9,10} The short-range order of the silicon network is not directly probed by these techniques. However, the initial stages of the growth process have not been studied using Raman spectroscopy because of the difficulty of measuring scattering from ultrathin *a*-Si:H films. Although interference-enhanced Raman scattering is a useful technique for sensitive monitoring of small changes in thin films, its requirements of definite film-to-substrate thickness make it unsuitable for studying spectra as a function of thickness.¹¹ In this paper we report the thickness dependence of the Raman spectra of the ultrathin *a*-Si:H films and speculate about the microscopic mechanism of growth on the substrate.

The samples were made by the plasma-enhanced chemical-vapor-deposition (PECVD) technique. To obtain films of varying thicknesses under identical plasma

conditions, we used the triode technique to isolate the plasma from the substrates that were held perpendicular to the electrodes.¹² We could thus obtain samples of continuously varying thickness from the same run. The growth conditions are a silane (SiH_4) flow rate of 5 sccm (where sccm denotes standard cubic centimeters per minute), a gas pressure of 30 mTorr, a mesh bias voltage of -40 V, and a radio frequency (13.56 MHz) power density of 0.3 W/cm^2 . Corning 7059 glass was used as substrates. The thicknesses quoted in this paper are estimated from deposition rates measured by deposition of thicker samples under nominally identical conditions.

The Raman-scattering experiments were performed in a backscattering configuration at room temperature. The Ar^+ -ion laser at 2.41 eV was used as a light source. The Raman spectrometer consists of a position-sensitive photomultiplier ITT F4146M and a triple-stage spectrograph DILOR XY with a stigmatic optical correction.¹³ This system enabled us to measure the Raman spectra of very thin films. The spectrometer slit width was set to 100 μm , leading to a spectral resolution of 3 cm^{-1} .

Figure 1 shows the horizontal-horizontal (HH) Raman spectra of *a*-Si:H having various thicknesses. The Raman signal of the glass substrate has been subtracted. The TO peak intensity is normalized by the signal intensity from the substrate. We were able to detect the TO-phonon peak for films with thicknesses down to 1.6 nm, but the TO band intensity decreases suddenly at a thickness of 1.5 nm and we could observe no Raman peaks for thinner samples. The signal intensity of the TO band has been plotted as a function of thickness in Fig. 2. The signal intensity is observed to increase in thickness and saturate at a thickness of ~ 2 nm. This saturation behavior is not well understood at present and needs further investigation.

Figure 3 shows the differential spectra of some of the samples in Fig. 1, obtained by subtracting the Raman spectrum of the bulk sample. At a thickness of 1.7 nm, the TO band is shifted to higher energy from the bulk position and a shoulder on the higher-frequency side is observed in the differential spectrum. As the film thickness increases from 1.7 to 20.6 nm, the shoulder on the higher-frequency side becomes smaller. Another shoulder on the lower-frequency side appears at a thickness of 2.0 nm and grows with thickness. The 20.6-nm-thick sample has only the shoulder on the lower-frequency side.

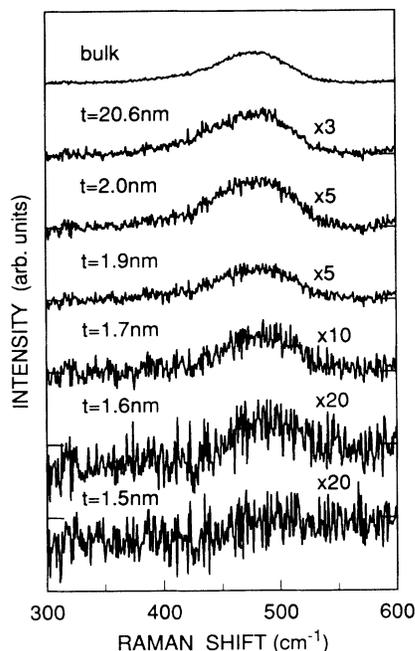


FIG. 1. HH Raman spectra of *a*-Si:H films of various thicknesses. The signal from the glass substrate has been subtracted.

From these Raman spectra, we may speculate on the microscopic process at the initial stages of growth on the glass substrate. Spectroscopic ellipsometry results have been modeled using small islands of material that grow and coalesce to form a continuous film with consequent reduction of void-volume fraction.^{9,10} We note that since void-rich material was found to show no shift of the TO mode frequency,¹⁴ the changes of void morphology during the initial film formation process would not be expected to affect the TO band. Another ellipsometry study finds that the imaginary part of the dielectric function in samples of similar thickness are blueshifted compared to bulk spectra.¹⁵ This was explained as being due to a hydrogen-rich layer at the interface, as has also been deduced from infrared spectroscopy.^{7,8} However, the TO mode has been found to be unaffected by the hydrogen content in PECVD films³ and, therefore, we do not expect the hydrogen content of the interface layer to

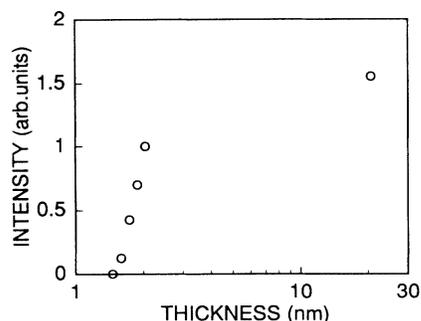


FIG. 2. The thickness dependence of the peak intensity of the Raman TO band.

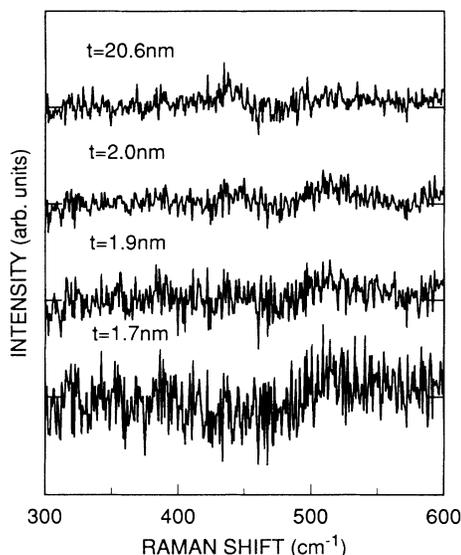


FIG. 3. Differential Raman spectra of *a*-Si:H of various thicknesses compared with the bulk spectrum.

influence the TO mode in our spectra. Kinetic ellipsometry studies suggest that the material initially deposited on glass is chemically modified.¹⁶ The formation of SiO_x could be a reason for the absence of the silicon TO mode in samples thinner than 1.5 nm (Fig. 2). As growth proceeds, a sufficient number of Si-Si bonds are formed and then we begin to observe the TO band. Since the islands initially formed on the glass substrate are rather small and the silicon network within is relatively unstrained, we might expect the TO peak to be shifted to the higher-energy side as seen in Fig. 3. This is also similar to that observed under high pressure.⁶ As growth proceeds further, the islands are connected with each other and a continuous *a*-Si:H film is created. During the coalescence process, the silicon network would become strained because each island is rigidly bound to the substrate. Since this strain would be larger than the strain in the bulk film, the TO peak would be shifted to the lower-frequency side, as observed at thicknesses of 2.0 and 20.6 nm in Fig. 3. The smoothing of substrate-determined film-surface roughness has been observed by spectroscopic ellipsometry and attributed to coalescence of islands.¹⁰ Thus, with continued growth, the strain would be expected to reduce. This leads to the disappearance of the low-frequency component of the TO band in thick films.

In summary, we have observed the Raman spectra of the ultrathin films of *a*-Si:H for the first time. The increase of the Raman intensity at some critical thickness and the appearance of high- and low-frequency components in the TO band at different thicknesses have been shown to be consistent with and complementary to previous studies of the initial stages of *a*-Si:H growth.

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