

Hydrogen-induced platelets in silicon: Infrared absorption and Raman scattering

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(Received 3 February 1992)

The local vibrational modes of hydrogen-induced platelets in crystalline silicon have been studied using infrared absorption and Raman-scattering spectroscopy. Four overlapping but distinct bands are observed in the region $2000\text{--}2200\text{ cm}^{-1}$. Hydrogen-isotope substitution confirms that these are hydrogen-related stretching vibrations. Hydrogen concentrations obtained from the integrated infrared band intensities are comparable to total hydrogen concentrations obtained from secondary-ion mass spectroscopy. Relative intensities of the bands depend on sample history and can be varied by annealing. This indicates that the four bands arise from at least three distinct structures. Polarization-sensitive Raman measurements indicate that the Raman-active local modes transform according to the fully symmetric representation of a trigonal point group. One structure possesses distinct ir and Raman-active local modes. We conclude that the platelets are highly ordered structures with fundamental building blocks consisting of silicon atoms with one hydrogen-saturated bond, and that at least one inversion-symmetric structure exists. We compare our results with previously proposed structures.

I. INTRODUCTION

Hydrogen, introduced into single-crystal silicon at moderate temperatures (e.g., $\leq 250^\circ\text{C}$), can generate extended structural defects.¹ These defects are planar in shape, are aligned predominantly along $\{111\}$ crystallographic planes, and involve the coordinated formation of Si-H bonds.² It has recently been demonstrated that the growth of hydrogen-induced platelets can be controlled independently of the nucleation process.³ In qualitative agreement with classical nucleation theory, platelet generation appears to involve the precipitation of a two-dimensional silicon hydride phase from a supersaturated solution of hydrogen in silicon. The remarkable two-dimensionality of platelets, over diameters of many tens of nanometers, suggests that the growth of the Si-H phase involves a highly anisotropic interaction between migrating hydrogen and platelets. While several theoretical models have been proposed for the structure of platelets,⁴⁻⁷ experimental information on the local bonding geometry has not been available. In this paper, we present results from both infrared absorption and Raman-scattering studies of the local vibrational modes (LVM's) that are associated with hydrogen-induced platelets. The properties of the local vibrational modes are predominantly determined by the microscopic structure in the first and second nearest-neighbor shells around the

hydrogen atoms. Therefore, these measurements provide direct information on the microscopic structure of the platelets. The results are used to evaluate the theoretically proposed models.

II. EXPERIMENT

Sample preparation techniques have been described in a previous article³ and will only be summarized here. n -type [100] FZ silicon ($[P] = 8 \times 10^{17}\text{ cm}^{-3}$) samples were hydrogenated by a remote hydrogen plasma at 150°C for 20 min followed by 275°C for 60 min. This two-step process has been shown by secondary-ion mass spectroscopy (SIMS) to introduce areal densities of H as high as $3 \times 10^{15}\text{ cm}^{-2}$. Transmission electron microscopy (TEM) reveals a high density of platelets oriented along $\{111\}$ planes within 100–200 nm of the sample surface. These samples are opaque to light of wavelength $\geq 7\text{ }\mu\text{m}$ due to strong free-carrier absorption. Therefore, n^+ epi/undoped [100] Cz silicon samples were also hydrogenated and studied.

Infrared absorption (ir) spectra were obtained with a Digilab 80-E Fourier transform spectrometer. Resolution was typically set to 4 cm^{-1} . Higher-resolution measurements did not further resolve the broad observed structures. A continuous flow helium cryostat allowed measurements between room temperature and 5 K. A

thermal infrared detector (TGS) was chosen because of its superb linearity, which is useful in observing broad bands. Absorption spectra were referenced to spectra obtained from control samples cut from the same starting wafers. Control samples were also hydrogenated, and then etched to remove approximately $1\ \mu\text{m}$ of material.

Room-temperature measurements of the unpolarized Raman scattering were performed in a backscattering geometry. The focused beam (514.5 nm) from an argon-ion laser was incident on the sample at 45° to the normal, and the scattered light was analyzed with a three-stage spectrometer and a photomultiplier detector. Polarized Raman spectra were collected in a pseudobackscattering geometry with the laser (488 nm) incident at 60° from the sample normal. The laser power was 100 mW and the spot size was $10\ \mu\text{m}$. A single grating spectrometer and a microchannel plate photomultiplier were used to disperse and detect the Raman-scattered light; a holographic interference notch filter was used to suppress elastically scattered light. Polarized spectra were corrected for differences in grating efficiency by calibration with a white light source. The spectral resolution was $4\ \text{cm}^{-1}$. The polarization geometry is defined with respect to the sample surface ([100]): the x , y , and z axes are parallel to [100], [010], and [001], while y' and z' axes are parallel to [01 $\bar{1}$] and [011].

III. RESULTS

Two broad peaks centered at 2065 and $2125\ \text{cm}^{-1}$ (bands I and III) are observed in ir and Raman spectroscopy after plasma hydrogenation [Figs. 1 and 2(a)]. Additional unresolved lines may lie between the features. No line narrowing or shift is observed between 300 and 5 K. As shown in Fig. 1, lower trace, isotopic substitution of deuterium for hydrogen shifts the peak positions to 1505 and $1550\ \text{cm}^{-1}$, respectively. The peak positions and isotopic shift are characteristic of Si-H stretching modes. The ir absorption cross section of the Si-H stretch vibration in $a\text{-Si:H}$ is known.⁸ From this value, areal densities of Si-H bonds of up to $5 \times 10^{15}\ \text{cm}^{-2}$ are obtained, in good agreement with total H concentrations in similar samples measured by SIMS. No other H-related modes are observed between 700 and $4000\ \text{cm}^{-1}$. No distinct H-D combination modes are observed in samples exposed to a 50% H, 50% D plasma. A previously reported¹ mode at $1960\ \text{cm}^{-1}$ was observed in both hydrogenated and control samples, and is attributed to a fourth-order Si phonon.

We present complementary ir and Raman measurements of the platelet-related Si-H stretching band in the same sample as a function of annealing (Fig. 2). The relative intensities of bands I and III vary with annealing, and two distinct modes appear at frequencies $2075\ \text{cm}^{-1}$ (IIa) and $2095\ \text{cm}^{-1}$ (IIb), in the ir spectra and Raman spectra, respectively. Bands I and III are dominant in as-hydrogenated samples [Fig. 2(a)]. After a 300°C anneal [Fig. 2(b)], bands IIa and IIb dominate, while band I is diminished and is visible as a shoulder on IIa (ir) or IIb (Raman). Bands IIa and IIb are attenuated by a 400°C anneal [Fig. 2(c)]. Band III is not substantially reduced

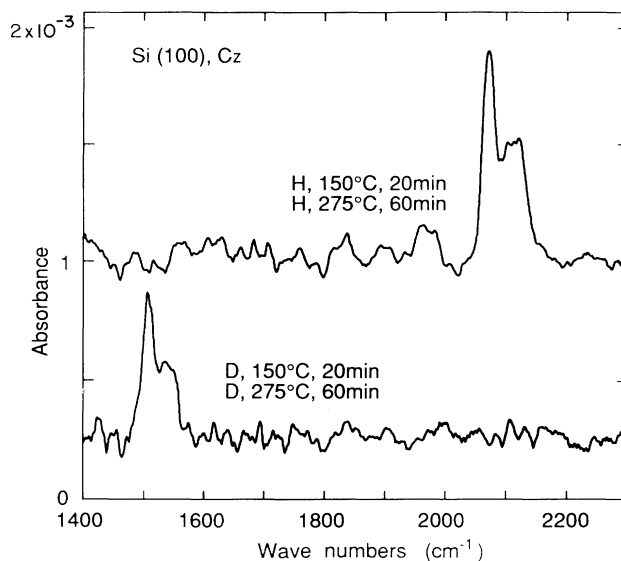


FIG. 1. Infrared-absorption spectra of hydrogenated and deuterated n^+ epi/undoped Cz silicon. A slowly varying background has been subtracted from both spectra. The ratio of the platelet-related local vibrational mode frequencies is approximately equal to the square root of the ratio of the reduced isotopic masses of hydrogen and deuterium.

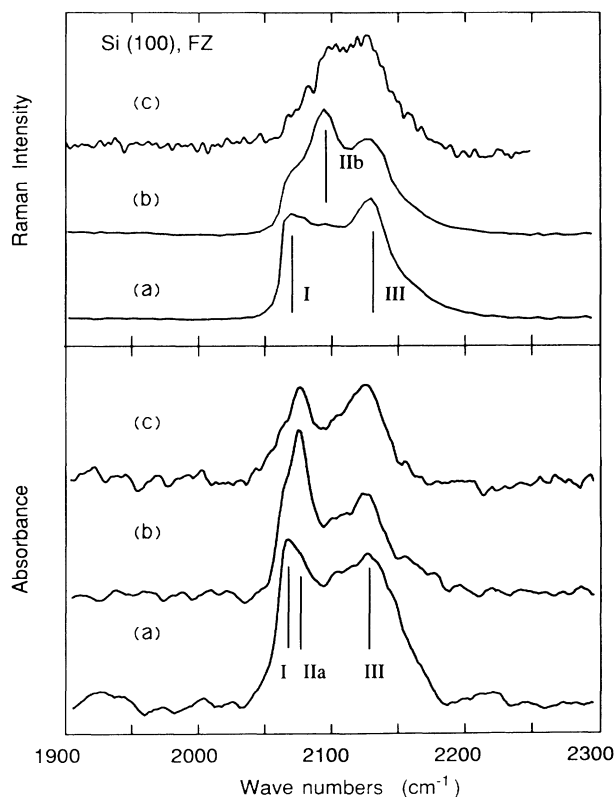


FIG. 2. Raman and infrared measurements of the platelet local vibrational modes in the same FZ n -Si sample as a function of annealing. (a) After exposure to a hydrogen plasma for 150°C (20 min) and 275°C (60 min). (b) An additional vacuum anneal at 300°C (30 min). (c) An additional vacuum anneal at 400°C (40 min). Distinct ir- and Raman-active modes (IIa and IIb) are observable after the 300°C anneal.

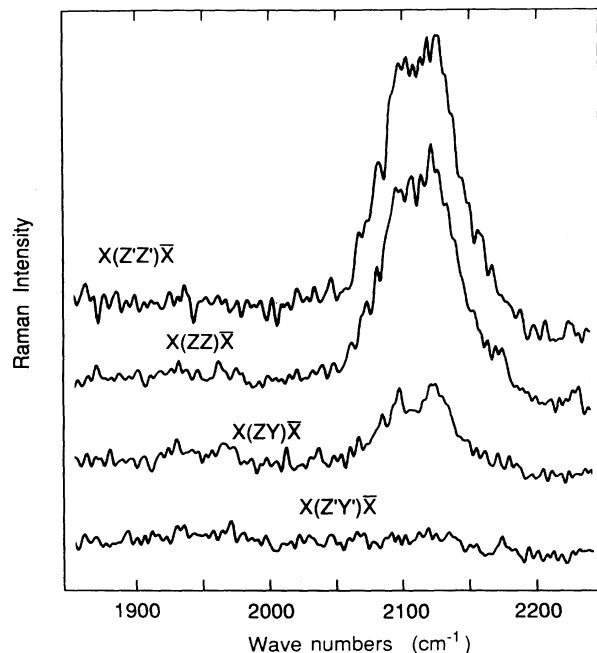


FIG. 3. Polarized Raman measurements of hydrogen-induced platelets in *n*-type FZ silicon (annealed at 400 °C) showing intensity as a function of incident and scattered light polarization. Polarization geometry is defined with respect to the sample surface ([100]). Spectra are offset vertically for clarity.

by annealing at temperatures below 450 °C (~60 min). These results are consistent with previous Raman measurements of the influence of annealing on the platelet local vibrational mode.³

Polarization-sensitive Raman spectra of an annealed (400 °C) hydrogenated sample are shown in Fig. 3. The Si-H stretch band is most intense in the $[x(z'z')\bar{x}]$ geometry, and is reduced by >95% in the $[x(z'y')\bar{x}]$ geometry.⁹ The shape of the band does not change with polarization. The polarization dependence of both the Si-H and Si-D LVM's measured in an unannealed sample exposed to a 50% H, 50% D plasma were identical. These measurements establish that all three Raman-active modes (I, IIb, III) obey the same polarization selection rules.

IV. DISCUSSION

The agreement between hydrogen concentrations determined by ir-band intensities and by SIMS establishes that most of the hydrogen present in our samples is incorporated in Si-H bonds. The large, temperature-independent bandwidths indicate inhomogeneous broadening that is most likely due to a range of platelet diameters. The absence of sharp hydrogen-related LVM's shows that the areal concentration of ir-active hydrogen-related point defects is below 10^{13} cm^{-2} .

The relative intensities of bands I and III depend on the sample history, and vary independently of bands IIa and IIb. The intensities of IIa and IIb appear correlated. This indicates that the four bands arise from at least three distinct structures (I, II, and III) whose populations

may be varied independently. Formation of structures I and III is clearly favored during the hydrogenation process ($T \leq 275 \text{ °C}$). The reduction in intensity of band I, and increase in IIa and IIb following a 300 °C anneal, indicate that structure I is metastable and suggests a transformation between structures I and II. Bands IIa and IIb are reduced by an anneal at 400 °C. There is no clear evidence of transformations from either structures I or II to III. Structure III is the most stable configuration observed.

V. CONCLUSION

LVM's probe the environment in the first and second nearest-neighbor shells around the hydrogen atoms. Selection rules for polarized Raman scattering at tetrahedral, trigonal, orthorhombic, and monoclinic centers may be obtained in a straightforward fashion.¹⁰ Our results are consistent only with a fully symmetric (A_1) mode at a trigonal center. All other modes of a trigonal center, and modes of lower point group symmetry, predict a finite scattering intensity in the $[x(z'y')\bar{x}]$ geometry, and are thus inconsistent with experiment. The symmetry of a {111}-oriented platelet cannot be higher than trigonal (i.e., tetrahedral). The bond-stretching vibration of silicon with one hydrogen-saturated bond (Si-H) satisfies the symmetry requirements. Other reasonable structures do not: Si-H₂ is not trigonal; Si-H₃ and ∇H_4 (vacancy with four hydrogen saturated bonds) both possess non- A_1 Raman-active vibrational modes in the Si-H bond-stretching region. We conclude that Si-H is the fundamental building block of all {111}-oriented platelet structures. Trigonal symmetry also indicates that these Si-H bonds are aligned along the platelet axis.

The Raman and ir intensities of band I as well as band III vary proportionally with annealing, indicating that these two structures (I, III) each have a mode that is both Raman and ir active. Bands IIa (ir) and IIb (Raman) also track with annealing. This suggests that there exists a structure (II) which possesses distinct Raman- and ir-active modes. Only inversion-symmetric centers may possess a Raman-active A_1 mode and distinct ir- and Raman-active modes. We conclude that structure II is inversion symmetric, with band IIa (IIb) corresponding to the odd (even) -parity vibrational mode.

Total-energy calculations have identified⁴⁻⁷ five low-energy platelet structures: (a) hydrogen molecules located at the interstitial sites between two {111} silicon planes; (b) hydrogen saturation of the Si-Si bonds at a {111} plane, forming one Si-H bond per atom; (c) removal of one double layer of Si atoms with hydrogen saturation of the dangling bonds (two per atom); (d) a double layer of metastable interstitial hydrogen (H_2^+) pairs; and (e) a hydrogenated half-stacking fault defect. An additional model has been suggested to explain recent high-resolution TEM measurements¹¹ of the lattice spacing at platelets: (f) saturation of Si-Si bonds between {111} planes having three bonds per atom. Finally, the similarity between the platelet Raman signature and hydrogen-related stretching modes attributed¹² to Si-H_{*n*} ($n = 1, 2, 3$)

complexes in α -Si:H has been noted,¹³ suggesting (g) a locally disordered platelet structure containing silicon atoms with one, two, and three hydrogen-saturated bonds.

The ir and Raman observations of Si-H stretching modes are inconsistent with (a), an interstitial molecular hydrogen platelet. The polarized Raman measurements rule out three additional models. Model (f) consists of Si-H₃ groups, which should exhibit an observable *E*-symmetry Si-H stretching mode. A disordered hydrogenated layer (g) will contain orthorhombic Si-H₂ groups as well as Si-H₃ groups. In model (b), we may assume that the H atoms relax away from the Si-Si bond directions, forming a staggered arrangement. Substantial relaxation of H atoms away from the Si-Si axes will break the local trigonal symmetry. However, we note that the hydrogen may be dynamic at the measurement temperature (300 K), and in this case the trigonal symmetry will be restored.

The three remaining proposed structures, the hydrogen-saturated double vacancy layer (c), the (d) metastable dihydrogen complex double layer (H₂^{*})^(d), and the half-stacking fault platelet (e), are trigonal structures characterized by Si-H bonding. (c) and (d) possess inversion symmetry, while (e) does not. Calculated vibrational spectra⁴ for models (d) and (e) may be compared with experiment. The stretching mode spectrum of (e) is predicted to consist of two modes separated by approximately 250 cm⁻¹. We do not observe such a doublet. It has been noted that the half-stacking fault defect has a high activation energy for formation. We conclude that (e) is not observed in our measurements.

The calculated stretching mode spectrum of (d), the metastable dihydrogen double layer, also consists of a

doublet. However, the mode separation depends strongly on the platelet diameter. The calculated frequency of the lower-energy mode varies over a range of about 400 cm⁻¹, as the platelet diameter changes from 0 to 100 nm, while the upper mode is not altered. Conceivably, this may make the lower-energy mode too broad to be observed. We conclude that models (c) and (d) are consistent with the results of our measurements.

We have made infrared transmission, Raman, and polarization-sensitive Raman measurements of the LVM's associated with {111} planar hydrogen-induced defects in silicon. The LVM's provide information about the local symmetry and bonding of hydrogen at platelets. Annealing studies indicate that at least three distinct structures exist. Polarized Raman measurements indicate that all Raman-active LVM's are fully symmetric vibrations at trigonal centers, corresponding to bond-stretching modes at silicon atoms with one hydrogen-saturated bond. One structure appears to possess distinct ir- and Raman-active modes, indicating inversion symmetry. Our results are compatible with two proposed models for the platelets: the metastable dihydrogen complex double layer (H₂^{*})^(d), and a H-saturated double vacancy layer. A third structure, H saturation of the Si-Si bonds at a {111} plane, is also consistent with experiment if the H atoms are allowed to reorient between equivalent off-axis positions.

ACKNOWLEDGMENTS

The authors wish to acknowledge informative discussions with W. Walukiewicz, L. M. Falicov, and C. Herring. This work was supported in part by NSF Grant Nos. DMR-88-06756 and DMR-91-15856.

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