PHYSICAL REVIEW B VOLUME 26, NUMBER 2 15 JULY 1982

Surface optical phonons and hydrogen chemisorption on polar and nonpolar faces of GaAs, InP, and GaP

L. H. Dubois and G. P. Schwartz
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 31 March 1982)

Surface optical phonons have been detected on both the polar (100) and nonpolar (110) faces of GaAs, InP, and GaP with the use of high-resolution electron-energy-loss spectroscopy. The observed frequencies (GaAs: 291, InP: 337, GaP: 396 cm^{-1}) on all surfaces are in excellent agreement (within 5 cm^{-1}) with theoretical predictions and were found to be independent of crystal face, bulk doping level, or method of sample preparation (cleavage in UHV versus sputter-annealing). The insensitivity of the surface-optical-phonon frequencies to the details of surface orientation, reconstruction, and near-surface stoichiometry is a consequence of the effective depth of atomic displacements ($\sim$200 Å) which contribute to the time-dependent electrostatic potential outside the crystal. Adsorption of atomic hydrogen results in identifiable modes for the Ga-H, As-H, In-H, and P-H stretching vibrations at approximately 1880, 2110, 1700, and 2350 cm^{-1}, respectively.

I. INTRODUCTION

Nearly 17 year ago Fuchs and Kliewer[1] predicted the existence of surface optical (SO) phonons in materials lacking a center of inversion symmetry. Subsequently, a simple expression for the frequency of the surface optical phonon was derived.[2] This expression was based on a description of the solid in terms of an isotropic, frequency-dependent dielectric constant which was assumed to be unaltered by the presence of the surface. Neither the effects of surface orientation nor the manner in which surface disorder or a surface variation from bulk stoichiometry were addressed by this theory. The recent advent of high-resolution electron-energy-loss spectroscopy (ELS) provides a probe of surface-optical phonons via the interaction of the Coulomb field of the incoming electron with the time-dependent electrostatic potential generated in the vacuum by atomic displacements beneath the surface of the solid. To date, the only data available to test the assumptions and general validity of this formalism on III-V compound semiconductors have been experiments by Matz and Lüth on vacuum-cleaved GaAs(110).[3] Although excellent agreement between theoretically derived and experimentally determined surface-optical-phonon frequencies was obtained in that work, questions remained concerning the mode frequencies on polar surfaces which cannot be obtained by cleavage in vacuum.

The current studies examine both the polar (100) and nonpolar (110) faces of GaAs, InP, and GaP (100 only) prepared by sputter-annealing techniques. High-resolution electron-energy-loss spectroscopy as well as Auger electron spectroscopy and low-energy electron diffraction (LEED) were performed to assess both the quality of the surface and to measure the surface-optical-phonon spectrum. The observed frequencies on all surfaces were in excellent agreement (within 5 cm^{-1}) with theoretical predictions and were found to be independent of the crystal orientation, bulk doping level, or method of surface preparation [cleavage in ultrahigh vacuum (UHV) versus sputter-annealing]. These findings can be rationalized in terms of the relative depths associated with surface disorder or reconstruction compared to the depth over which atomic displacements contribute to the time-dependent electrostatic potential outside the crystal. Concurrent chemisorption studies involving atomic hydrogen and deuterium resulted in the identification and assignment of modes related to the Ga-, As-, In-, and P-H stretching frequencies on the surface between 1700 and 2350 cm^{-1}. The relative intensity of these modes was sensitive to the surface stoichiometry.

II. EXPERIMENTAL

All experiments were carried out in a diffusion and titanium sublimation pumped ultrahigh vacu-

 ©1982 The American Physical Society

TABLE I. Summary of LEED, Auger, and high-resolution ELS data for GaAs, InP, and GaP.

Substrate	Orientation	Doping	LEED pattern	Auger peak-height ratio	ω_{SO} (cm^{-1})	I_1/I_0
GaAs	(110)[a,b]	Cr (semi-insulating)			292±2	0.35±0.10
	(110)	Zn: $N_A \sim 1\times10^{18}$ cm^{-3} (*p* type)	(1×1)	$I_{Ga(1070\ eV)}/I_{As(1220\ eV)}=1.19\pm0.06$	290±5	0.16±0.01
	(100)[c]	Cr (semi-insulating)	(4×1)-45° Ga-rich surface	1.40±0.04	291±5	0.12±0.02
InP	(110)	S: $N_D \sim 2\times10^{18}$ cm^{-3} (degenerate)	(1×1)	$I_{In(404\ eV)}/I_{P(120\ eV)}=1.2\pm0.06$	337±5	0.20±0.02
	(100)	Fe (semi-insulating)	(4×1)-45° In-rich surface	1.39±0.06	338±5	0.20±0.02
	(100)	undoped: $N_D \sim 1\times10^{16}$ cm^{-3}	(4×1)-45° In-rich surface	1.43±0.08	336±5	0.16±0.01
	(100)	S: $N_D \sim 2\times10^{18}$ cm^{-3} (degenerate)	(4×1)-45° In-rich surface	1.44±0.08	336±5	0.17±0.01
GaP	(100)	undoped: $N_D \sim 1\times10^{16}$ cm^{-3}	(4×1)-45° Ga-rich surface	$I_{Ga(1070\ eV)}/I_{P(120\ eV)}=0.17\pm0.01$	396±5	0.15±0.01

[a]Reference 3.
[b]Sample prepared by cleavage in UHV, all other samples were prepared by hydrogen ion sputtering and annealing.
[c]Extensive sample charging periodically observed.

um chamber with a base pressure near 1×10^{-11} Torr. The system was equipped for high-resolution electron-energy-loss spectroscopy, Auger electron spectroscopy, low-energy electron diffraction, thermal desorption mass spectrometry, and ion sputtering. The design of the high-resolution ELS spectrometer is similar to that of Sexton.[4] For these experiments the incident-electron angle (60° to the surface normal) and energy ($\sim$4 eV) were held constant and electrons were only collected in the specular direction. The elastic scattering peak from a clean semiconductor surface had a maximum intensity near 5×10^4 counts per second and a full width at half maximum (FWHM) which ranged from 50 to 120 cm^{-1}, depending on the details of surface preparation. For surfaces with adsorbed hydrogen, the scattering intensity was reduced by as much as an order of magnitude and the width of the elastic peak increased by 20–50 cm^{-1}. All spectra were recorded at $\sim$300 K.

Samples were polished to a mirror finish using a bromine-methanol mixture (final concentration $\sim$0.5 vol. % Br) and etched in 1:1 HF:H_2O at room temperature prior to mounting in the UHV chamber. Table I contains details of the orientation and doping of the samples used in this study. A total of 18 crystals were examined to ensure reproducibility. Clean GaAs, InP, and GaP surfaces were obtained by hydrogen ion sputtering at 500–1000 eV for a total of 30 min followed by annealing at 690–750 K for 1–2 h. This cleaning procedure left the surface free of S, C, or O contaminants. H_2 (rather than argon) was chosen as the sputtering gas to minimize the formation of Ga and/or In islands.[5] However, raising the surface temperature above $\sim$780 K or annealing samples for more than 3–4 h caused the surface to irreversibly mottle or haze. Although the exact origin of this discoloration is not known, it is believed to be due to the loss of As or P with subsequent formation of either Ga or In islands.[5,6] It was noted that the most intense ELS spectra and the sharpest LEED patterns were observed just prior to and during the initial stages of discoloration. The quality of both ELS and LEED spectra rapidly degraded if annealing was continued much beyond the initial observation of a surface haze.

Dosing surfaces with hydrogen or deuterium occurred with both the ionization gauge and mass spectrometer filaments on. Atomic H and D are the presumed species which bond to the semiconductor surfaces since neither molecular H_2 nor D_2 readily adsorb at room temperature.[7]

III. RESULTS

A. Clean semiconductor surfaces

1. GaAs

The results of LEED, Auger, and high-resolution ELS measurements on (110) and (100) surfaces of GaAs are summarized in Table I. The ELS data of Matz and Lüth[3] for vacuum-cleaved GaAs(110) are included for comparison. Our observed LEED patterns are consistent with previous reports for (110) (Ref. 6) and Ga-stabilized (100) surfaces.[8] Comparison of the (110) and (100) GaAs *LMM* Auger ratios ($I_{Ga(1070\ eV)}/I_{As(1220\ eV)}$) corroborates that the (100) surface being examined is a Ga rather than an As-stabilized surface.

On the bare (110) substrate produced by cleavage in UHV, Matz and Lüth[3] reported a surface-optical-phonon frequency of 292 cm^{-1} (1 meV $\simeq$8.065 cm^{-1}) and were able to observe up to three overtones of this mode which extended out to nearly 1200 cm^{-1}. Our own data on clean (110) and (100) surfaces which were sputter-annealed indicate no substantial shift in the surface-optical-phonon frequency within experimental error (Table I). A typical high-resolution ELS spectrum of Cr-doped GaAs (100) is presented in Fig. 1. The elastic peak full width at half maximum (50 cm^{-1}) observed in this study is somewhat better than the 90–110 cm^{-1} reported in Ref. 3, but the intensity ratio of

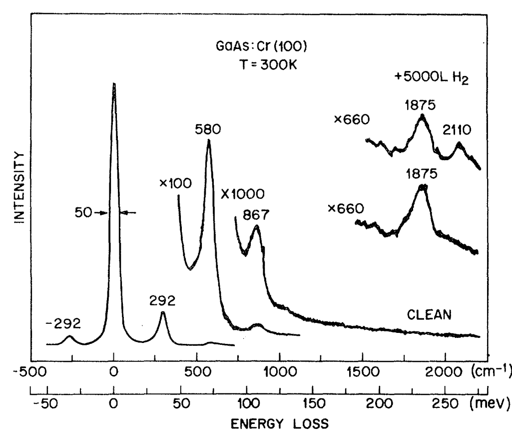

FIG. 1. Surface-optical-phonon spectrum of a clean, Cr-doped GaAs(100) single crystal showing two overtones of the fundamental peak (580, 867 cm^{-1}) and a single energy-gain peak (-292 cm^{-1}). The inset shows vibrational spectra of adsorbed atomic hydrogen on lightly (upper trace) and heavily (lower trace) annealed samples.

the surface optical phonon to the elastic peak is consistently higher (~0.35) on their cleaved samples compared to our sputter-annealed wafers (~0.12). Consequently we were only able to unambiguously observe two overtones of the surface optical phonon (580, 867 cm^{-1}). The mode to the left of the elastic peak in Fig. 1 (-292 cm^{-1}) is due to electrons that have gained energy from thermally excited phonons.[9]

2. *InP*

High-resolution ELS spectra of single-crystal indium phosphide have not been reported previously. A compilation of our results for LEED, Auger, and ELS measurements on sputter-annealed (110) and (100) InP surfaces with carrier concentrations ranging from compensated to degenerate are presented in Table I. The observed LEED patterns are those associated with the (1×1) (110) (Ref. 6) and In-rich (4×1)-45° (100) (Ref. 8) surfaces. Typical Auger spectra from the (100) and (110) surfaces are shown in Fig. 2. The comparison of the In(404 eV)/P(120 eV) ratios between the (110) and (100) substrates substantiate that the (100) surface is In rich.

Representative high-resolution ELS spectra of clean, compensated InP(100) and heavily S-doped InP(110) are shown in Figs. 3 and 4, respectively. Within experimental error (±5 cm^{-1}), the observed surface-optical-phonon frequencies (336–338 cm^{-1}) are identical on all of the (110) and (100) faces studied and are also independent of bulk doping (see Table I). Three overtones of the surface optical phonon (675, 1018, 1351 cm^{-1}) as well as two energy-gain peaks (-338, -670 cm^{-1}) are observed. On most of the InP samples studies to date, the surface optical phonon to elastic peak intensity ratio (I_1/I_0) is ~0.2; i.e., somewhat better than we observe on GaAs, but significantly lower than the ratio observed by Matz and Lüth on cleaved GaAs.[3]

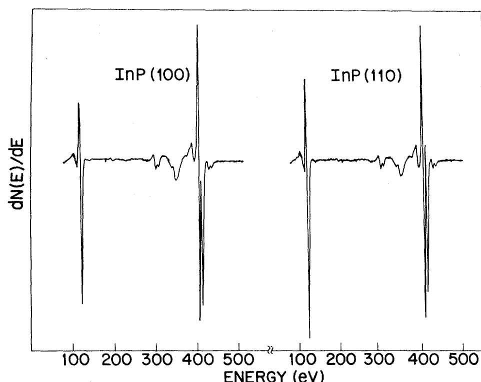

FIG. 2. Auger-electron spectra of clean (100) (left curve) and (110) (right curve) Fe-doped InP. The incident voltage and current were 3 kV and 10 μA, respectively.

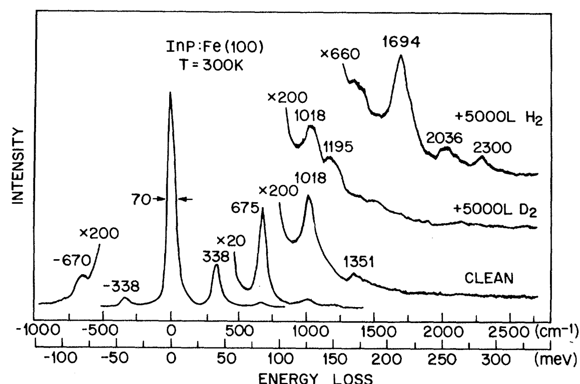

FIG. 3. Composite high-resolution electron-energy-loss spectra of clean (lower trace) and hydrogen (deuterium) exposed (upper two traces) InP(100). The intensity of the peaks is plotted in Fig. 5.

3. *GaP*

LEED, Auger, and high-resolution ELS results for clean GaP(100) are summarized in Table I. A well-ordered (4×1)-45° LEED (Ref. 8) pattern was much more difficult to obtain on this surface and consequently higher annealing temperatures and longer annealing times (more than 3 h) were required. The frequency of the observed surface-optical-phonon band at 396 ±5 cm^{-1} is independent of surface order, however. The GaP surface faceted above ~870 K, causing a decrease in the elastic

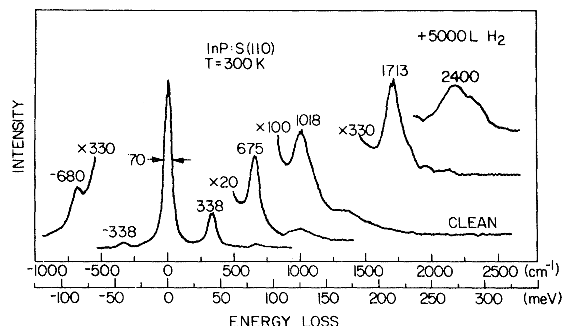

FIG. 4. Surface-optical-phonon spectrum of clean S-doped InP(110). The inset shows vibrational spectra of adsorbed atomic hydrogen. The mode at ~1700 cm^{-1} was observed on all spectra while the broad band centered near 2400 cm^{-1} was only found on lightly annealed samples.

TABLE II. Hydrogen (deuterium) chemisorption on GaAs and InP.

Sample	Observed frequencies (cm^{-1})	Assignment
GaAs(110)[a]	1890±5 (1380±10)	Ga-H (Ga-D) stretch
	2150±10 (1660±20)	As-H (As-D) stretch
GaAs(100)	1875±20	Ga-H stretch
	2110±25[b]	As-H stretch
InP(110)	1710±20 (1140)	In-H (In-D) stretch
	~2400 (broad)	P-H stretch
InP(100)	1694±20 (1195±25)	In-H (In-D) stretch
	2036±25	
	2300±25 (1600–1650)	P-H (P-D) stretch

[a]References 3 and 8.
[b]Peak intensity dependent on annealing time; peak disappears on well-annealed samples.

peak intensity, an increase in the elastic peak width, but no change in the surface-optical-phonon frequency.

B. Hydrogen chemisorption

1. GaAs

Atomic hydrogen (deuterium) adsorption on vacuum-cleaved GaAs(110) was previously studied by Matz and Lüth.[7] They reported two modes at 1890 (1380) and 2150 (1660) cm^{-1} which were assigned to Ga-H (Ga-D) and As-H (As-D) stretching vibrations (see Table II). We find atomic hydrogen adsorption on Cr-doped GaAs(100) to be very sensitive to the annealing conditions. On lightly (~1 h) annealed surfaces two features around 1875 and 2110 cm^{-1} are observed after exposing the clean surface to 5000 L of H_2 at room temperature. These features are shown in the inset in Fig. 1. With additional annealing, the I_{Ga}/I_{As} Auger ratio increases to its final value of ~1.40, and the intensity of the 2110 cm^{-1} feature decreases to the noise level. No evidence for adsorbed molecular hydrogen ($\hbar\omega = 4159$ cm^{-1}) is found.

2. InP

Atomic hydrogen (deuterium) adsorption on all surfaces of indium phosphide is also very sensitive to the annealing conditions. Exposure of a heavily S-doped InP(110) crystal to 5000 L of H_2 (D_2) at room temperature results in two distinct modes. A peak at ~1710 (~1140) cm^{-1} is always present, independent of surface preparation. The frequency of this mode varies ±20 cm^{-1} from sample to sample presumably due to slight differences in both surface preparation and in gas exposure. A broad band centered near 2400 cm^{-1} is also observed on lightly annealed samples. This mode could be completely removed on samples which had discolored due to prolonged heating. However, well-ordered LEED patterns and intense ELS spectra were still observed at this point. These results are shown in the inset in Fig. 4 and are summarized in Table II.

Adsorption of atomic hydrogen and deuterium has also been studied on the (100) surface of InP. In this case three peaks are observed at 1694, 2031–2046, and 2300 cm^{-1}, as seen in the inset in Fig. 3. Although the intensity of the 1694-cm^{-1} peak is always considerably greater than the two peaks above 2000 cm^{-1}, extended annealing at 670–690 K was never effective in totally removing those signals. The ratio of the 2036 to 2300 cm^{-1} peak intensities was observed to fluctuate and as a general observation, the 2036-cm^{-1} peak was either comparable or more intense than the feature at 2300 cm^{-1}. For atomic deuterium adsorption, only a single weak mode around 1195 cm^{-1} is observed (see inset, Fig. 3), although in some of our spectra there is marginal evidence for another mode between 1600 and 1650 cm^{-1}. Again, no evidence for adsorbed molecular hydrogen (deuterium) is found on either face of InP.

3. GaP

The relatively low elastic peak intensity (~2000 c/sec) taken in conjunction with a further reduc-

tion in signal intensity by a factor of 8−10 following hydrogen chemisorption precluded adsorption studies of H_2 and D_2 on these samples.

IV. DISCUSSION

A. Clean semiconductor surfaces

The frequency of the surface optical phonon can be obtained by solving Laplace's equation for the electrostatic potential and applying the appropriate surface boundary conditions [$\epsilon(\omega_{SO})=-1$].[2] For a dielectric constant $\epsilon(\omega)$ given by Eq. (1),

$$\epsilon(\omega)=\epsilon_\infty+\frac{(\epsilon_s+\epsilon_\infty)\omega_{TO}^2}{\omega_{TO}^2-\omega^2}\ , \tag{1}$$

where ϵ_s and ϵ_∞ are the static and high-frequency dielectric constants and ω_{TO} the bulk transverse-optical-phonon frequency, the frequency of the surface optical phonon (ω_{SO}) is given by

$$\omega_{SO}=\omega_{TO}\left[\frac{\epsilon_s+1}{\epsilon_\infty+1}\right]^{1/2} . \tag{2}$$

The derivation of Eq. (2) assumes that the dielectric constant is both isotropic and uniform right up to the solid-vacuum interface, i.e., no account is taken of variations either in the surface vibrations present at different crystal faces nor the stoichiometry changes induced in the near-surface region during sample preparation. A comparison of the measured surface-optical-phonon frequency with the calculated values (Table III) indicates that neither the crystal face nor the noted differences in surface stoichiometry strongly perturb the observed frequencies. Even samples that had faceted due to prolonged annealing displayed no reproducible shift in ω_{SO}. For GaAs, the measured and calculated frequencies agree within 2 cm^{-1}; for the InP and GaP the agreement is within 5 cm^{-1}. Both sets of results are within the experimental errors

TABLE III. Comparison of measured and calculated surface-optical-phonon frequencies.

Substrate	Dielectric constants ϵ_S	ϵ_∞	ω_{TO} (cm^{-1})	ω_{SO} (cm^{-1}) Calc.[a]	Meas.
GaAs	12.91	10.91	269	290.7	291±5
InP	12.38	9.55	304	342.4	337±5
GaP	11.10	9.11	366.3	400.7	396±5

[a]From Eq. (2).

associated with measuring the mode frequencies and establishing the dielectric constants.

The apparent insensitivity of the surface-optical-phonon frequencies to variations in the near-surface region can be understood in terms of an "effective" sampling depth defined by $|Q_{\parallel}|^{-1}$, the electron momentum transfer parallel to the surface.[2,3] This depth can be estimated from Eq. (3):

$$|Q_{\parallel}|^{-1}\sim[k_0(\hbar\omega_{SO}/2E_0)\sin\theta]^{-1}\ , \tag{3}$$

where k_0 is the wave vector of the incoming electron at energy E_0 and scattering angle θ. For our samples we estimate $|Q_{\parallel}|^{-1}$ to be between 180 and 260 Å. The perturbation of the first few monolayers of either the reconstructed (110) or group-III stabilized (100) surfaces is thus small compared to the region which contributes to the bulk of the time-dependent electric field. As a consequence, neither surface disorder nor faceting strongly effect the observed surface-optical-phonon frequencies.

One further point should be noted concerning the frequency of the observed modes. The dielectric function of Eq. (1) is not appropriate in situations where there is a high free-carrier concentration. Matz and Lüth have already examined heavily n-doped GaAs(110) using high-resolution electron-energy-loss spectroscopy and observed conduction-band surface plasmons.[10] We have not observed similar phenomena on any of our samples. For p-type crystals [our GaAs(110)], the effective mass of holes (M_h) is large, and the plasma frequency ω_p given by

$$\omega_p^2=ne^2/\epsilon_\infty M_h \tag{4}$$

is too low to couple efficiently to the bulk phonon frequencies in order to form a coupled plasmon-phonon mode. However, we also examined both InP (110) and (100) samples which were heavily sulfur doped ($n\sim2-5\times10^{18}$ cm^{-3}) and were able to obtain spectra in which only surface optical phonons rather than plasmon-phonon coupled modes were observed. This could only occur if the carrier concentration within a depth of $|Q_{\parallel}|^{-1}$ of the surface was strongly depleted.

Two mechanisms will contribute to this carrier depletion. The first involves depletion of the dopant atoms (sulfur) in the near-surface region (∼200 Å) due to the sputter-annealing process used in sample preparation. The second entails band bending induced by surface states which are present following sputter-annealing, even on (110) surfaces. These defect-induced, acceptorlike sur-

face states bend the bands upward on n-type GaAs(110) and InP(110), thereby depleting n-type samples of carriers in the near-surface region. On (100) surfaces, intrinsic as well as defect-induced surface states contribute to upward band bending.[11] Estimates of the depletion width W at zero applied bias can be obtained from

$$W=\left[\frac{2\epsilon_s}{eN_D}\left[V_d-\frac{kT}{e}\right]\right]^{1/2}, \tag{5}$$

where N_D is the bulk carrier concentration, V_d is the diffusion potential (0.7–0.8 eV for GaAs and 0.4–0.5 eV for InP),[12] and ϵ_s the dielectric permittivity of the substrate. The calculated depletion widths are of order 100–250 Å, depending on the bulk doping level [$(2-5)\times 10^{18}$ cm^{-3}] and the material under study.

One sample of heavily doped (S, $n \sim 2\times 10^{18}$ cm^{-3}) InP(100) was irradiated with white light focused onto the surface from a 75-W xenon discharge lamp. No differences were observed between surface-optical-phonon spectra collected under these conditions and in the dark. This result indicates that either there was insufficient light to affect an appreciable flattening of the bands or, more likely, that dopant depletion had occurred. Recent secondary ion mass spectroscopy (SIMS) studies have observed near-surface dopant depletion, particularly for Cr in GaAs.[13] We suspect that a combination of both mechanisms is operative in depleting carriers from a region within $|Q_{\parallel}|^{-1}$ of the surface, thereby allowing us to obtain spectra even on heavily doped samples.

Once the frequency of the surface optical phonons is known, the intensity of the observed vibrations can be calculated using expressions derived by several authors.[2,3] However, all of these derivations assume a perfectly ordered lattice—a poor assumption for our experiments due to the methods of surface preparation. Ibach has already shown that due to the finite acceptance angle of the high-resolution electron-energy-loss spectrometer, surface order can markedly affect the intensity of the observed energy-loss peaks.[14] On the other hand, the relative intensity of the overtone bands (I_n) is given by a Poisson distribution[2,9] and therefore should not be as sensitive to surface order. Representative data for clean InP(100) are shown in Fig. 5(a). The intensity of the energy-gain peaks (I_{-n}) should also be sensitive to surface order. However, one can relate I_{-n} to the intensity of the energy-loss peaks by a Boltzmann factor.[2,5] Data for compensated InP(100) are plotted in Fig. 5(b).

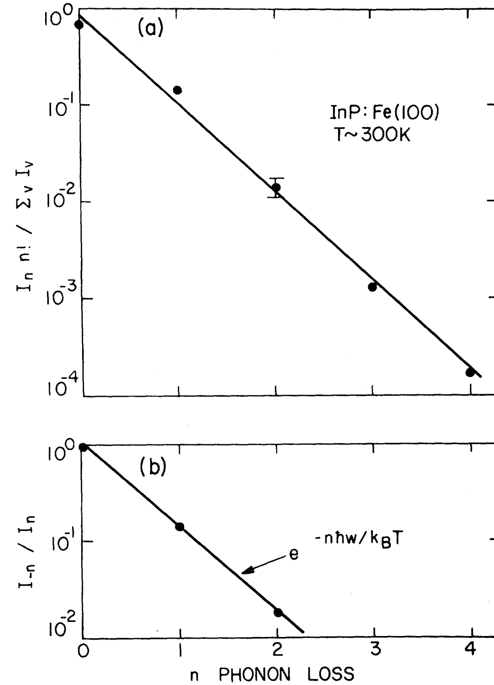

FIG. 5. (a) Poisson distribution of the measured loss intensities for Fe-doped InP(100) at ~300 K. The data are taken from Fig. 3. The error bar is a typical variational from run to run. (b) Plot of the ratio of the nth phonon gain to the nth phonon loss vs n. The straight line is calculated with $\hbar\omega = 338$ cm^{-1}.

B. Hydrogen chemisorption

1. GaAs

Matz and Lüth have previously studied the vibrational spectrum of hydrogen (deuterium) adsorbed on vacuum-cleaved GaAs(110) and assigned bands at 1980 (1380) and 2150 (1660) cm^{-1} to Ga-H (Ga-D) and As-H (As-D) stretching vibrations by analogy with suitable model compounds.[7] Thus on the Ga-rich (100) face of GaAs one expects only a single mode near 1900 cm^{-1}. However, if the surface is slightly roughened and other crystal planes are exposed, one expects to see some intensity in the As-H stretch. This is precisely what Fig. 2 shows: a single peak at 1875 cm^{-1} on well-annealed samples and a second peak at 2110 cm^{-1} on a roughened surface. Differences in the observed vibrational frequencies on the (100) and (110) surfaces may be caused either by changes in the surface stoichiometry or by variations in the hydrogen coverage. At present we have no simple method of relating the H_2 exposure (5000 L) to the actual amount of atomic H evolved on various hot filaments within the vacuum system.

2. InP

By analogy with hydrogen chemisorption on GaAs, one expects two modes (In-H and P-H) on InP(110) and only a single mode (In-H) on the In-rich (100) face. However, surface preparation was observed to alter the adsorbed hydrogen vibrational spectrum on InP significantly. The assignment of the weak 2300−2400 (1600−1650) cm^{-1} mode observed on both InP(100) and (110) to the P-H (P-D) stretch is reasonably direct by comparison with stretching vibrations (cm^{-1}) in the molecules PH(2275), PD(1653) (Ref. 15) and PH_3(2325), PD_3(1690).[16] The strength of the feature at 1694 cm^{-1} on InP(100) taken in conjunction with the fact that this surface is In rich suggests that this mode be assigned to the In-H stretch. It is considerably more difficult, however, to find model compounds which bracket this region of the spectrum. Diatomic indium hydride InH is reported to have a stretching frequency around 1450 cm^{-1},[15] in poor agreement with the present data. We were unable to find any data for compounds of the form R_2InH or similar useful analogs. Data do exist, however, for the related tin complexes (R_3SnH, R_2SnH_2, and $RSnH_3$, $R=C_2H_5$, C_3H_7, and C_4H_9). In this series, the Sn-H stretching frequency varies between 1797 and 1862 cm^{-1}.[17] The observed value of 1694 cm^{-1} is seen to be a reasonable assignment for the In-H stretching frequency since metal-hydrogen stretching frequencies generally decrease as one moves to the left and down in the Periodic Table.[15,17]

The peak observed at 1195 cm^{-1} from the absorption of 5000 L of D_2 on InP(100) at room temperature (see Fig. 3) corresponds closely to the value anticipated for the In-D stretch (1198 cm^{-1}) under the assumption that the frequency should scale as $(M_H/M_D)^{1/2}$ on a solid surface for which the reduced masses are just those of H and D, respectively. These assignments are consistent with the effects of surface preparation on the observed vibrational spectra. On lightly annealed samples both In-H and P-H stretching vibrations are observed (their relative intensities depending on the surface stoichiometry), while on samples which have been extensively annealed, the In-H stretch predominates.

The mode observed around 2031−2046 cm^{-1} on InP(100) has not been assigned unambiguously. Since this mode never disappears completely, even on well-annealed samples where the 2300-cm^{-1} intensity is nearly at the noise level, it was initially thought to represent a combination mode involving the In-H stretch and a surface phonon ($1694+337=2031$ cm^{-1}). Subsequent experiments on InP(110) failed to show evidence for this mode. Alternatively, the mode around ~2035 cm^{-1} may represent a distinct binding site involving either In or P which is never completely removed by annealing, or a more complex motion distinct from a simple symmetric stretch normal to the surface. At present, one cannot distinguish between these two possibilities, although the absence of this mode on InP(110) suggests a preference for the latter explanation. Finally, all of our mode assignments are summarized in Table II.

V. SUMMARY

Surface optical phonons have been studied on the sputter-annealed (110) and (100) faces of GaAs, InP, and GaP. The observed frequencies are independent of the crystal face, bulk doping, or method of sample preparation (cleavage in UHV versus sputter-annealing). Neither the reconstructed atomic positions on the (110) nor the Ga- and/or In-rich surface layer on the (100) samples strongly perturbs the measured frequencies. These findings are consistent with the physical origin of the surface modes emanating from a depth proportional to $|Q_{||}|^{-1}$. No surface phonon-plasmon coupling has been observed indicating that even in the case of heavily S-doped samples the near-surface region was effectively depleted of carriers.

Hydrogen (deuterium) absorption on InP suggests an assignment of In-H (In-D) and P-H (P-D) stretching frequencies of 1694−1710 (1140−1195) and 2300−2400 (1600−1650) cm^{-1}, respectively, with the intensity of all of these modes sensitive to the method of surface preparation. An additional persistent mode at ~2035 cm^{-1} for H_2 adsorbed on InP(100) cannot be assigned at this time. Observation of modes due to Ga-H (1875) and As-H (2110 cm^{-1}) stretching variations are consistent with the previous assignments of Matz and Lüth.

ACKNOWLEDGMENTS

It is a pleasure to thank W. A. Bonner for providing the InP substrates, A. C. Gossard for the *p*-doped sample of GaAs(110), and D. L. Allara for the loan of equipment during the course of part of these experiments.

[1]R. Fuchs and K. L. Kliewer, Phys. Rev. 140, A2076 (1965).
[2]See, for example, D. L. Mills, Prog. Surf. Sci. 8, 143 (1977) and references therein.
[3]R. Matz and H. Lüth, Suppl. Le Vide, Les Couches Minces 201, 762 (1980).
[4]B. A. Sexton, J. Vac. Sci. Technol. 16, 1033 (1979).
[5]D. K. Skinner, J. Electron. Mater. 9, 67 (1980).
[6]A. U. MacRae and G. W. Gobelli, J. Appl. Phys. 35, 1629 (1964).
[7]H. Lüth and R. Matz, Phys. Rev. Lett. 46, 1652 (1981).
[8]C. R. Bayliss and D. L. Kirk, J. Phys. D 9, 233 (1976).
[9]H. Ibach, Phys. Rev. Lett. 24, 1416 (1970).
[10]R. Matz and H. Lüth, Phys. Rev. Lett. 46, 500 (1981).
[11]J. Massies, P. Devoldere, and N. T. Linh, J. Vac. Sci. Technol. 16, 1244 (1979).
[12]W. E. Spicer, I. Lindau, P. Skeath, and C. Y. Su, J. Vac. Sci. Technol. 17, 1019 (1980).
[13]T. J. Magee, J. Peng, J. D. Hong, C. A. Evans, Jr., V. R. Deline, and R. M. Malbon, Appl. Phys. Lett. 35, 277 (1979).
[14]H. Ibach, Sur. Sci. 66, 56 (1977).
[15]K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
[16]T. Shimanouchi, *Tables of Molecular Vibrational Frequencies,* Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand. (U.S.) Circ. No. 39 (U.S. GPO, Washington, D.C., 1972), Vol. I.
[17]E. Maslowsky, Jr., *Vibrational Spectra of Organometallic Compounds* (Wiley, New York, 1977).