

## Observations of phonon line broadening in the III-V semiconductors by surface reflection Raman scattering\*

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By means of surface reflection Raman scattering the dependence of the  $q = 0$  TO- and LO-phonon line shapes on surface preparation in the compounds GaAs, InAs, GaSb, and InP has been investigated. Polished surfaces have broad phonon lines compared to etched, annealed, or cleaved surfaces. We show that phonon line broadening is a consequence of microscopic disorder generated during the polishing process. Temperature-dependence studies of phonon linewidths in polished and annealed GaAs surfaces demonstrate that the additional broadening observed in the polished surfaces is caused by a temperature-independent process. We conclude that the additional line broadening in the polished surfaces is caused mainly by inhomogeneous shifting of the phonon frequencies due to inhomogeneous strain near the sample surface. A secondary mechanism for phonon line broadening is increased phonon anharmonic decay in polished surfaces caused by local lowering of lattice symmetry in damaged surface layers. We observed that phonon line shapes in cleaved, etched, and 0.05- $\mu\text{m}$  polished GaAs surfaces narrow as the optical skin depth of the exciting laser is increased; phonon lines in similarly prepared InAs surfaces broaden as the skin depth is increased. From this observation it is concluded that the magnitude of the strain in surface layers is peaked at  $\approx 500 \text{ \AA}$  below the surface. The strain decreases beyond this depth and also relaxes to a lower value toward the surface.

### I. INTRODUCTION

The surface optical properties of many classes of solids have been observed to be strongly dependent on the methods used to prepare sample surfaces. Many experimenters have reported variations in the optical properties of the III-V compounds and group IV element materials for various surface preparations. For example, the absorption spectra in GaAs become distorted if the sample has been mechanically polished, but these distortions do not appear if the sample has a cleaved (110) face.<sup>1</sup> Jones and Hilton<sup>2</sup> reported a variation in the infrared reflectance of GaAs between samples mechanically polished and those chemically etched. From their observations of the reflectance spectra they proposed that the depth of damage in mechanically polished surfaces was at least as large as the size of the final polishing powder. Warekois *et al.*<sup>3</sup> reached a similar conclusion about the extent of the surface damage in polished GaAs surfaces. The intensity of the reflectance spectra of Ge in the region 2650–10 000  $\text{\AA}$  was observed<sup>4</sup> to depend on surface quality. The highest reflectance observed was for electropolished faces, and the fine structure in the reflectance spectra observed in this surface was not observed for surfaces with mechanically polished faces. The damage done on GaAs surfaces by argon-ion implantation has been observed<sup>5</sup> as variations in the fine structure of the reflectance spectra. Light-scattering experiments have shown that the linewidths of the phonon spectra in the intermetallic compounds AuAl<sub>2</sub>, AuGa<sub>2</sub>, and AuIn<sub>2</sub><sup>6</sup> are dependent on the method used to prepare the sample surfaces; the linewidths seem to depend

on the size of the final polishing powder. Most recently, Karpol and Pratt<sup>7</sup> observed a dependence of the photoluminescence in  $n$ -type GaAs on the surface preparation. For surfaces polished with larger polishing powder size the intensity of the photoluminescence decreased. Also, the shape and location of emission lines in the spectrum were affected by the surface treatment.

We noticed<sup>8</sup> a difference in the phonon spectra between a (111) mechanically polished surface of GaAs and a cleaved (110) surface. The TO- and LO-phonon lines observed by surface reflection Raman scattering from the (111) polished face were broader than the TO-phonon line observed from the (110) cleaved face. Polishing a cleaved (110) face in the same manner also gave a broad TO-phonon line shape. We concluded from this observation, that the difference in the phonon spectra for the two surfaces was not due to differences between the (110) and (111) crystal orientations, but that phonon spectra were dependent on the differences between mechanically polished and cleaved surfaces. For this reason, we conducted an extensive study of the dependence of the phonon spectra in the III-V compounds on the methods used to prepare the surface. The aim of the study was to determine the cause of phonon line broadening in polished samples and to correlate Raman data with those obtained by other techniques of measuring the properties of damaged surfaces.

### II. EXPERIMENTAL

We performed a typical Raman experiment in the back-scattering geometry illustrated in Fig. 1. The Raman source was an argon-ion laser with the

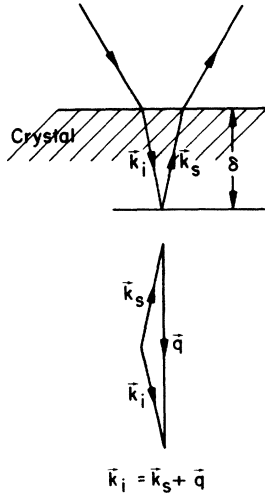


FIG. 1. Backscattering geometry and momentum conservation for Stokes scattering.

outputs at 4579, 4765, 4880, 4965, and 5145 Å. The incident light was polarized in the plane of incidence, and the polarization of the scattered light was not analyzed. The angle of incidence for the exciting laser beam was adjusted to correspond to Brewster's angle by minimizing the reflected-light intensity. Thus the laser power entering the penetration depth was maximized, and by this adjust-

$$F_2(x) = \begin{bmatrix} 2a & 0 & 0 \\ 0 & -a & 0 \\ 0 & 0 & -a \end{bmatrix}; \quad F_2(y) = \begin{bmatrix} 0 & -a & 0 \\ -a & 0 & \sqrt{2}a \\ 0 & \sqrt{2}a & 0 \end{bmatrix}; \quad F_2(z) = \begin{bmatrix} 0 & 0 & -a \\ 0 & \sqrt{2}a & 0 \\ -a & 0 & -\sqrt{2}a \end{bmatrix}.$$

Because the index of refraction for these materials is so large, the wave vectors for the incident and scattered light inside the crystal are nearly along the direction normal to the surface. Momentum conservation for Stokes scattering as illustrated in Fig. 1 then requires the phonon wave vector to be also along the direction normal to the surface. For back scattering from the (111) crystal face, we thus observed scattering from both the TO and LO phonons; for back scattering from the (110) crystal face only the scattering from the TO phonon is observed.

The sample surfaces we studied were prepared by mechanical polishing, chemical etching, and annealing. Mechanical polishing was done by mounting the sample on a polishing tool which was held against a rotating wheel of variable angular speed while a fine slurry graded away the sample face. Polishing started with alumina powder of 1.0- $\mu\text{m}$  grit size on a silk fiber cloth on the wheel.

ment, we could enhance the scattered-light intensity by several times. Scattered light was collected in the direction normal to the crystal surface with a 10-cm-focal-length converging lens and analyzed with a Spex 1400 double-grating spectrometer. The diffracted light was detected by an ITT FW 130 photomultiplier with an S-20 cathode, and the number of photon counts was digitally recorded by a computer-controlled data-accumulation system.<sup>9</sup> Typical integration time per data point was about 90 sec.

The samples we studied were wafers of GaAs, InAs, GaSb, and InP purchased from Monsanto Co. with oriented (111) faces. The GaAs sample was an undoped high resistivity ( $\rho = 4.3 \times 10^6 \Omega \text{cm}$ ) slice; GaSb was undoped  $p$  type with carrier concentration of  $2.3 \times 10^{17}/\text{cm}^3$ ; and InAs was undoped  $n$  type with carrier concentration about  $2.6 \times 10^{16}/\text{cm}^3$ . These slices were all single crystalline and we were able to prepare good (110) faces in these materials by cleavage in air. The InP sample was polycrystalline, so it could not be cleaved.

Because these crystals are all opaque to incident visible light, surface-reflection Raman scattering is a convenient method of studying the properties of the phonons in the thin layer near the surface of the crystal, the optical skin depth. A convenient set of orthogonal axes for our samples was  $\hat{x} \parallel [111]$ ,  $\hat{y} \parallel [1\bar{1}0]$ , and  $\hat{z} \parallel [11\bar{2}]$ . The Raman tensors for the  $F_2$  modes which we observed take the following form with respect to these axes<sup>10</sup>:

After the surface was polished well with this abrasive (usually only a few minutes of polishing time) polishing continued on a different silk cloth with 0.3- $\mu\text{m}$  alumina. The final polishing was with 0.05- $\mu\text{m}$  alumina powder on a felt microcloth. Each stage of the polishing was of sufficient duration to remove completely the damaged layer from the previous polish, and the sample and polishing tools were washed in distilled water between each polishing stage to remove all traces of the alumina abrasive.

Samples were chemically etched in several different solutions. The fastest etch was a 1:1 mixture of bromine in methanol. Typical etching time was about 1 min. A solution of 1 HF: 1 HNO<sub>3</sub>: 1 H<sub>2</sub>O was also used, and samples etched in this mixture gave similar Raman spectra. For this reason, the studies of the phonon spectra were all based on the etch solution of bromine and methanol.

Annealing was done in a small furnace capable of

achieving any temperature between 200 and 1000 °C. All samples were annealed in an atmosphere of flowing helium gas to prevent contamination of the surface by oxygen or nitrogen adsorption. Typical annealing time was about 20 min and the normal operating furnace temperature was 550 °C.

### III. EXPERIMENTAL RESULTS: GaAs

Presented in Fig. 2 are the phonon spectra for GaAs for the different surface preparations of (a) mechanical polishing with 0.05- $\mu\text{m}$  powder, (b) polishing and etching in bromine and methanol, (c) polishing and annealing at 550 °C, and (d) cleavage. These data were taken with the 4880- $\text{\AA}$  argon line as the exciting source, and the samples were at room temperature. The Raman lines for the polished face are broader than those for the other three surfaces. The data indicate that etching and annealing a polished surface provide a surface which has nearly the same Raman spectra as a cleaved (110) face.

To understand further how mechanical polishing changes the shape of the phonon spectra, we studied samples polished with different polishing powder size. Figure 3 shows the change in phonon linewidths for different polishing powder size for the grits 1.0, 0.3, and 0.05  $\mu\text{m}$ . It was impossible to obtain good Raman spectra for samples polished with powder size larger than 1.0  $\mu\text{m}$  because of the intense diffuse reflection from the sample surface. If we assume that surface damage extends as deep as the size of the polishing powder, surfaces po-

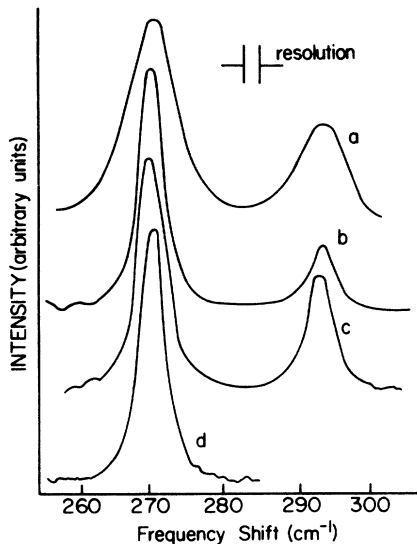


FIG. 2. GaAs phonon spectra for surfaces prepared by (a) 0.05- $\mu\text{m}$  powder polishing, (b) polishing and then etching in bromine and methanol, (c) polishing and annealing at 550 °C, and (d) cleavage. The peak at 270  $\text{cm}^{-1}$  is  $\omega_{\text{TO}}$ ; the peak at 293  $\text{cm}^{-1}$  is  $\omega_{\text{LO}}$ .

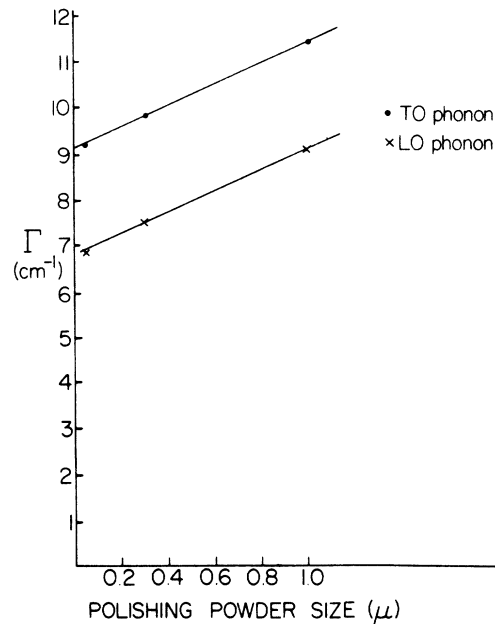


FIG. 3. Dependence of GaAs phonon linewidth on polishing powder size.

lished with 1.0 and 0.3- $\mu\text{m}$  powder are more extensively damaged than a surface polished with 0.05- $\mu\text{m}$  powder. Phonon-line-broadening mechanisms are enhanced in these more damaged surfaces.

With a high-resolution Olympus metallurgical microscope, we were able to observe the damage in polished surfaces and compare these surfaces with etched, annealed, and cleaved surfaces. Microscopic examination of polished surfaces revealed surface scratches of about 20- $\mu\text{m}$  length and 0.5- $\mu\text{m}$  width and surface pits of about 2  $\mu\text{m}$  diameter. The density of scratches and pits in the polished surfaces was greatest for the surface polished with 1.0- $\mu\text{m}$  powder and least in the 0.05- $\mu\text{m}$  polished surface. The etched and cleaved surfaces also showed observable scratches and pits under the microscope, but the densities of these damages were much lower than in any polished surface. The annealed surfaces had the same appearance under the microscope as the surface before annealing.

We studied the temperature dependence of GaAs phonon lines in a sample mechanically polished with 0.05- $\mu\text{m}$  powder and a similarly polished and then annealed surface. The intrinsic phonon linewidths for the TO and LO modes in these surfaces have been plotted as a function of temperature over the range of (4–300) °K in Figs. 4 and 5, respectively. The intrinsic phonon linewidths were obtained by removing the broadening of the data by

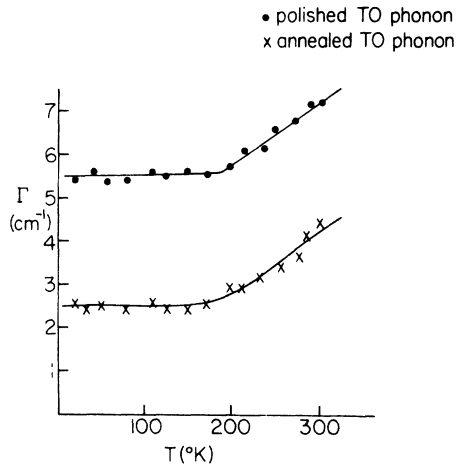


FIG. 4. Dependence of GaAs TO-phonon linewidth with temperature for polished and annealed surfaces.

the spectrometer slits from the measured phonon linewidths. We assumed that the slit profile was Lorentzian, and that the measured spectra were a convolution of this Lorentzian with the intrinsic Lorentzian phonon line shape. The observed line shape was fitted by the least-mean-square method to a Lorentzian profile with the line width  $\Gamma$  as an adjustable parameter.

The data in Figs. 4 and 5 demonstrate that phonon linewidths in polished and annealed surfaces stay constant over the temperature range (4–150) °K. Above 150 °K the phonon linewidths for both surfaces increase linearly with increasing temperature. The data also show that the difference in linewidths between the polished and annealed surfaces is nearly a constant, independent of temperature.

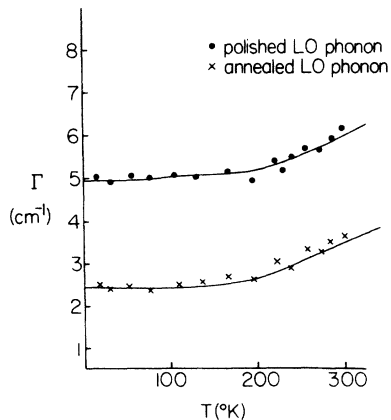


FIG. 5. Dependence of GaAs LO-phonon linewidth with temperature for polished and annealed surfaces.

#### IV. EXPERIMENTAL RESULTS: OTHER III-V SEMICONDUCTORS

To compare our previous results of phonon line broadening in polished GaAs surfaces, we studied similarly prepared surfaces of GaSb, InAs, and InP by surface-reflection Raman scattering. The measured values of phonon linewidths for the TO and LO modes in these materials for a variety of surface preparations are listed in Table I, and they can be compared with some of the earlier results for GaAs. The samples of InAs, GaSb, and InP were polished with 0.05- $\mu\text{m}$  alumina powder. The linewidths for the TO and LO modes for these polished surfaces were larger than the other surfaces studied. An etched InAs surface had a more narrow TO-phonon line than a polished surface, but the LO-phonon linewidth in the etched surface was about the same as that in the polished surface. A cleaved InAs surface had the most narrow TO-phonon line. The cleaved GaSb face had a more narrow TO-phonon line than the polished face, and in the polycrystalline InP sample the annealed surface had narrower phonon lines than the polished surface. The data indicate that surface-preparation techniques have a direct effect on the measured phonon linewidths in these other III-V compounds. Polished surfaces have larger phonon linewidths than etched, annealed, or cleaved surfaces. We also note that the relative magnitudes of the linewidths among the III-V compounds differ considerably.

We found that the phonon linewidth depends not only on the surface preparation, but also on the optical skin depth of the exciting radiation. The skin depth  $\delta$  at a wavelength  $\lambda$  is related to the extinction coefficient  $k$  through the relation

$$\delta = \lambda / 4\pi k.$$

By changing the wavelength of the exciting laser,

TABLE I. Measured phonon linewidths for GaAs, InAs, GaSb, and InP for different surface preparations.

		$\Gamma(\text{TO})^a$ ( $\text{cm}^{-1}$ )	$\Gamma(\text{LO})^a$ ( $\text{cm}^{-1}$ )
GaAs	polish	7.6	6.5
	etch	4.2	4.5
	anneal	5.7	4.2
	cleave	4.2	
InAs	polish	10.1	6.0
	etch	7.9	6.0
	cleave	7.1	
GaSb	polish	4.1	6.0
	cleave	3.1	
InP	polish	5.3	4.8
	anneal	4.8	2.6

<sup>a</sup>Line width measurements include spectrometer slit width of  $\approx 2 \text{ cm}^{-1}$ .

TABLE II. Values of the optical skin depth in GaAs for the different argon-ion-laser wavelengths. Values for  $k$  were obtained from the data of Sturge (Ref. 11).

$\lambda$ (Å)	$k$	$\delta = \lambda/4\pi k$ (Å)
4579	0.520	700
4765	0.490	780
4880	0.425	920
4965	0.412	970
5145	0.363	1140

we are therefore able to change the optical skin depth and sample by light-scattering phonons at different depths below the surface of a crystal. We have tabulated in Table II the skin depths in GaAs for the five argon laser wavelengths using the values for  $k$  obtained from the data of Sturge.<sup>11</sup> These skin depths range from 700 to 1140 Å. By varying the incident laser wavelength we can study the phonon spectra in differently prepared GaAs surfaces for different surface-layer depths. Plotted in Figs. 6 and 7 are the measured linewidths for the TO and LO phonons for samples polished with 1.0-, 0.3-, and 0.05- $\mu\text{m}$  polishing powder and etched and cleaved surfaces for the five different skin depths available with the argon laser. The phonon linewidths for the surfaces polished with 1.0- and 0.3- $\mu\text{m}$  powder size do not change, within the error of determining the linewidth, for the different skin depths. This is physically consistent with the hypothesis that the depth of damage done by mechanical polishing extends at least as deep as the size of the polishing powder size. The quality of these polished surfaces should be about the same and produce phonon linewidths which are essentially the same. However, for the 0.05- $\mu\text{m}$  polished surface and the etched and cleaved surfaces the phonon linewidths decrease with increasing skin depth.

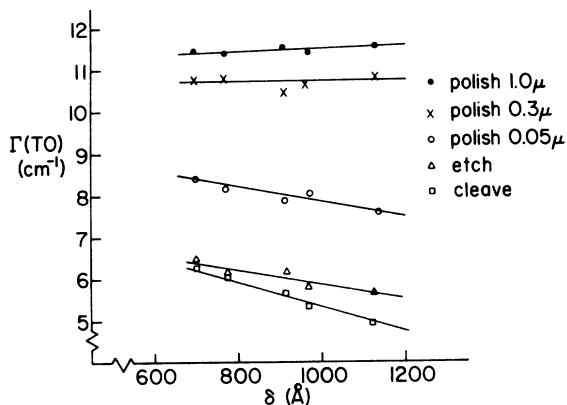


FIG. 6. Change in GaAs TO-phonon linewidth with optical skin depth for different surface preparations.

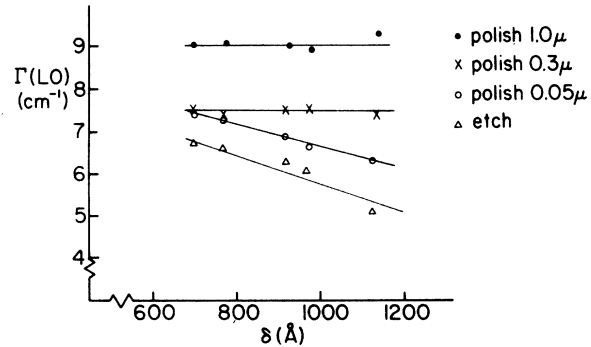


FIG. 7. Change in GaAs LO-phonon linewidth with optical skin depth for different surface preparations.

Using the data of Phillip and Ehrenreich<sup>12</sup> for the extinction coefficient of InAs, we have tabulated in Table III the optical skin depths for the five different argon laser lines in InAs. Because  $k$  is larger in InAs than in GaAs, the skin depths only cover the range  $\sim 200$ – $400$  Å. We studied InAs samples prepared by 0.3- $\mu\text{m}$  polishing, 0.05- $\mu\text{m}$  polishing, etching, and cleaving for the different argon lines 4579, 4880, and 5145 Å, and the measured linewidths for the TO and LO modes for these different skin depths are plotted in Figs. 8 and 9. Again we observe that for the 0.3- $\mu\text{m}$  polished face the measured phonon linewidths are constant for the three skin depths. This is the same observation as was made with GaAs. For the skin depths of 214 and 255 Å, the linewidths for the phonon modes in the other surfaces are nearly the same. However, when the skin depth is increased to 390 Å, the phonon linewidths are observed to increase. This increase in linewidth in the InAs surfaces is opposite to what is observed in the similarly prepared GaAs surfaces.

## V. DISCUSSION

As we demonstrated in Fig. 2, phonon lines in mechanically polished GaAs samples are broader than those observed in etched, annealed, and cleaved surfaces. Because surface-reflection

TABLE III. Values of the optical skin depth in InAs for the different argon-ion-laser wavelengths. Values for  $k$  were obtained from the data of Phillip and Ehrenreich (Ref. 12).

$\lambda$ (Å)	$k$	$\delta = \lambda/4\pi k$ (Å)
4579	1.70	214
4765	1.63	232
4880	1.52	255
4965	1.48	266
5145	1.05	390

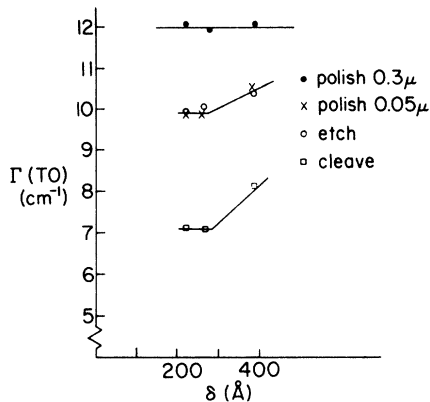


FIG. 8. Change in InAs TO-phonon linewidth with optical skin depth for different surface preparations.

Raman scattering samples mainly those phonons in the skin depth layer near the surface, we conclude that phonon line broadening in polished surfaces is a consequence of the macroscopic and/or microscopic damages in the skin-depth region generated during polishing. Macroscopic damages are the pits and scratches caused by the polishing powder, with an average size of about 500 Å for 0.05- $\mu$ m polishing powder. Accompanying these larger damaged areas are microscopic disorders in the forms of point defects and dislocations.

Macroscopic damages may produce broadened phonon lines if phonons scatter from the pits and scratches. This process could occur for phonons of any wavelength which see a damaged area large compared to the phonon wavelength; Sparks *et al.*<sup>13</sup> have proposed this type of macroscopic surface damage as the mechanism for the broadening of ferromagnetic resonance lines, and this mechanism for line broadening was experimentally verified in resonance studies for polished surfaces.

The microscopic damages generated during the polishing process can produce phonon line broadening in at least two ways. First, additional line broadening can occur because lattice symmetry is lowered in polished samples due to point defects and dislocations. Anharmonic decay and scattering processes which are not normally allowed in the undamaged lattice can become allowed when local symmetries are reduced, so that line broadening occurs because of increased anharmonic phonon decay and scatter channels. This increase in decay and scatter occurs primarily for phonons with short wavelengths comparable to the size of the microscopic disorder. Second, the observed phonon linewidths can increase due to the inhomogeneity of strain within the scattering volume. It is known that both TO- and LO-phonon frequencies change when a crystal is subjected to stress and

thereby to strain.<sup>14</sup> The frequency change of phonons with stress (or strain) was found to be linear within the accuracy of the measurements. Thus, if the scattering volume near the sample surface prepared by polishing contains regions of positive and negative strain, the phonon frequency in these different regions will shift both in the negative and positive directions with varying amount. Through this mechanism, the observed phonon widths in inhomogeneously strained samples can show inhomogeneous broadening due to shifting of the peak frequencies.

We reported above the observations of the appearance of the polished, etched, annealed, and cleaved surfaces under a microscope. Annealed surfaces have the same appearance under the microscope as the polished surface before annealing. Since annealed and etched surfaces have nearly the same Raman spectra, however, we are able to conclude that phonon line broadening by macroscopic damages in the surface is of secondary importance. Scattering of phonons by visible pits and scratches of  $\sim 1$ - $\mu$ m size on the surface are not the primary cause of the additional phonon broadening that we observe, rather phonon line broadening is primarily due to microscopic damages which are not observable under the microscope.

By comparing the linewidths for polished and annealed GaAs surfaces as a function of temperature, we are able to determine which mechanism due to microscopic disorder in a polished surface is responsible for phonon line broadening, that is, increased anharmonic decay and scattering channels due to reduced local symmetries or shifting of the peak frequency due to inhomogeneous strain. We can assume that the linewidths for the annealed surface are due primarily to anharmonic decay and scattering processes so that

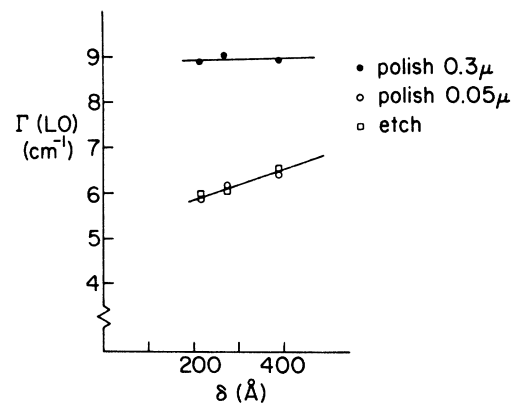


FIG. 9. Change in InAs LO-phonon linewidth with optical skin depth for different surface preparations.

$$\Gamma_{\text{anneal}} = \Gamma(T),$$

where  $\Gamma(T)$  depends on temperature through the Bose-Einstein occupation number of the phonons involved in the anharmonic decay and scatter. The linewidths for the polished surface also should depend on anharmonic decay and scatter but should have an additional contribution due to microscopic disorder in the polished-surface layer. Thus

$$\Gamma_{\text{polish}} = \Gamma(T) + \Gamma_{\text{disorder}}.$$

We then can write

$$\Gamma_{\text{disorder}} = \Gamma_{\text{polish}} - \Gamma_{\text{anneal}}.$$

Comparison of the variation in linewidth for both TO and LO modes in Figs. 4 and 5 for the polished and annealed surfaces shows that  $\Gamma_{\text{disorder}}$  is clearly independent of temperature, since  $\Gamma_{\text{polish}} - \Gamma_{\text{anneal}}$  is a constant, independent of  $T$ . This fact implies that the additional phonon line broadening in the polished surfaces,  $\Gamma_{\text{disorder}}$ , is not caused by increased decay and scattering channels in a damaged surface. If  $\Gamma_{\text{disorder}}$  were due to increased anharmonic decay and scattering channels, it should depend on the temperature. We conclude, therefore, that the mechanism for phonon line broadening we observe in polished surfaces is due to inhomogeneous strain broadening of resonance lines. We believe that the broad phonon lines we observe are the superposition of many Lorentzian phonon lines with their peaks shifted to higher and lower frequencies from the phonon frequencies of the strain-free regions. This conclusion is consistent with the observations of Weinstein and Cardona<sup>14</sup> of the effects of uniaxial stress on the Raman spectrum of GaAs. They reported that for compressive stress parallel to the (111) crystal face in undoped GaAs, the TO-phonon frequency shifted by 0.6% for stress magnitudes  $6 \times 10^9$  dyn/cm<sup>2</sup>. This is equivalent to shifts of  $1.6$  cm<sup>-1</sup>. Dilation and compression would thus produce phonon frequency shifts over a range of  $3.2$  cm<sup>-1</sup> for this magnitude of stress. The difference in TO-phonon linewidths between the polished and annealed samples is about  $3$  cm<sup>-1</sup> corresponding to a mean stress in the surface layer of about  $6 \times 10^9$  dyn/cm<sup>2</sup>. Weinstein and Cardona noted that undoped samples withstood stresses of  $10^{10}$  dyn/cm<sup>2</sup> before breaking. Since the polishing process does indeed "break" the crystal, we believe that a stress of this magnitude may be generated by polishing and relax to a mean value of  $\sim 10^9$  dyn/cm<sup>2</sup> in the layer near the surface. Because the low-temperature studies of phonon linewidths indicate anharmonic phonon decay is not greater in polished samples, we conclude that the phonon lines we observe are broadened by inhomogeneous strain due to microscopic disorder near the surface. The magnitude of the strain in

the surface layer, estimated by comparison with the work of Weinstein and Cardona, is realistic for stressed GaAs samples.

We reported in Sec. IV that the observed phonon linewidths in 0.05- $\mu$ m polished, etched, and cleaved GaAs surfaces decreased as the optical skin depth of the exciting light was increased by changing the wavelength, and that the phonon linewidths in similarly prepared InAs surfaces increased as the skin depth was increased. As we have concluded earlier, phonon lines are broadened primarily by shifting of the phonon frequency to higher and lower values due to inhomogeneous strain, and line broadening due to increased anharmonic phonon decay and scatter is a secondary contribution. The reason why phonon lines in GaAs surfaces narrow as the skin depth is increased is because the density of microscopic disorders decreased with increasing distance from the surface. Thus the magnitude of the inhomogeneous strain in the surface layer decreases with increasing distance from the surface. Phonon linewidths in 1.0- and 0.3- $\mu$ m powder-size polished surfaces are constant over the range of skin depths from 700 to 1140 Å, because the densities of disorders in these surfaces stay constant at these depths below the crystal surface. InAs phonon linewidths in a surface polished with 0.3- $\mu$ m power are also constant over the range of skin depths from  $\sim 200$  to 400 Å, suggesting that the density of disorders in this surface is constant at these different depths. We believe that InAs phonon lines in 0.05- $\mu$ m polished, etched, and cleaved surfaces at skin depths of  $\sim 200$  Å are more narrow than those at  $\sim 400$  Å below the surface because of strain relaxation at the surface. After the crystal is "broken" during polishing, strain at the surface can decrease and be less than the strain at deeper depths from the surface. This relaxation of inhomogeneous strain near the surface can produce more narrow InAs phonon lines at skin depths of  $\sim 200$  Å.

The GaAs data indicate that, at each optical skin depth, the magnitudes of the phonon linewidths are greatest for the surface polished with 1.0- $\mu$ m polish and decrease as the surface quality improves. We conclude that the density of microscopic disorder is greatest in the 1.0- $\mu$ m polished surface and decreases to its lowest value in the cleaved surface. By a similar analysis we found that the density of disorders in InAs samples is greatest in the 0.3- $\mu$ m polished surface and decreases to its lowest value in the cleaved surface.

The present study shows that by comparing phonon linewidths in different compounds prepared by different techniques a profile of the density of disorders in the surface layer of crystals and the extent of the inhomogeneous strain at different depths below the surface of a crystal can be obtained.

This is a new application of the light-scattering technique in the study of crystal surfaces.

#### VI. CONCLUSION

We have demonstrated by surface-reflection Raman scattering that phonon lines in the III-V semiconductors are broadened in polished samples due to inhomogeneous strain generated during the polishing process. The strain damage is removed by etching and annealing, and the phonon lines in these surfaces become more narrow than those observed in polished surfaces.

We also observed that the phonon lines in GaAs surfaces narrowed as the optical skin depth was increased, suggesting that the density of disorders causing the strain field is less at depths of  $\sim 1100$  Å than it is at  $\sim 700$  Å. We observed the opposite effect in InAs samples, and we believe this indicates that surface-layer strain fields relax at the surface and are less at  $\sim 200$  Å below the surface than they are at  $\sim 400$  Å from the surface.

The data presented in this paper indicate the

necessity of more quantitative measurements of phonon line broadening by inhomogeneous strain. Stress devices, such as those used by Weinstein and Cardona,<sup>14</sup> can be employed to determine more accurately the magnitudes of strain in surface layers of crystals.

Through the present study we have demonstrated that surface-reflection Raman scattering is a useful technique in studying the properties of phonons in the surface layers of crystals. For the first time, we have shown that light scattering can be used in a new application of measuring the extent of inhomogeneous strain in damaged surface layers.

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