



Space charge layers and hydrogen adsorption on the cleavage surfaces of III-V compound semiconductors
by Yu Chen

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Montana State University
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Abstract:

High resolution electron energy loss spectroscopy and other surface analytical techniques have been used to study the cleavage and lightly sputtered (110) surfaces of III-V compound semiconductors. Two aspects of their properties are investigated.

First, the conduction-band-electron plasmon and its coupling with the optical phonon in the space charge layer near the surface are studied. In the depletion layer, as the space charge layer forms, the energy positions of these coupled modes shift. In addition, the phonon in the depletion layer is unscreened due to the absence of electrons and oscillates at the uncoupled frequency. Thus three losses are observable. A two-layer model together with local response theory is employed to interpret the data successfully. Space charge parameters are obtained from the model calculation. In an accumulation layer, the plasmon is localized in the space charge region and also couples to the optical phonon. The shifts and intensity changes of these coupled modes are systematically measured as the space charge layer forms and the data are analyzed and understood in the context of model calculations. The high density of electrons in the accumulation layer screens the uncoupled phonon beneath it; thus the bare phonon cannot be observed, in contrast to the case of the depletion layer.

The second aspect is the study of hydrogen chemisorption processes on the cleavage and lightly sputtered surfaces. The H is observed to adsorb on both surface cation and anion atoms for GaAs, GaP and InP where H forms a bond with the dangling bonds. This picture is believed to be true for GaSb, InSb and InAs although quantitative conclusions could not be made. The effective charges for the H-substrate bonds of GaAs, GaP, and InP is calculated. An argument based on electronegativities of these elements is pursued to interpret the trend in the values of the effective charges. A general model to correlate the effective charge with the material's ionicity is proposed. On sputtered surfaces, the anion-H stretch intensity is enhanced relative to that of the cation-H stretch. The strongest enhancements occur on samples containing In, where the local In clustering due to sputtering is believed to be responsible for the passivation of surface In bonds.

**SPACE CHARGE LAYERS AND HYDROGEN
ADSORPTION ON THE CLEAVAGE SURFACES
OF III-V COMPOUND SEMICONDUCTORS**

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A thesis submitted in partial fulfillment
of the requirements for the degree

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APPROVAL

of a thesis submitted by

Yu Chen

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Approved for the Major Department

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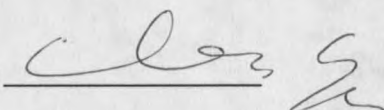
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ABSTRACT

High resolution electron energy loss spectroscopy and other surface analytical techniques have been used to study the cleavage and lightly sputtered (110) surfaces of III-V compound semiconductors. Two aspects of their properties are investigated.

First, the conduction-band-electron plasmon and its coupling with the optical phonon in the space charge layer near the surface are studied. In the depletion layer, as the space charge layer forms, the energy positions of these coupled modes shift. In addition, the phonon in the depletion layer is unscreened due to the absence of electrons and oscillates at the uncoupled frequency. Thus three losses are observable. A two-layer model together with local response theory is employed to interpret the data successfully. Space charge parameters are obtained from the model calculation. In an accumulation layer, the plasmon is localized in the space charge region and also couples to the optical phonon. The shifts and intensity changes of these coupled modes are systematically measured as the space charge layer forms and the data are analyzed and understood in the context of model calculations. The high density of electrons in the accumulation layer screens the uncoupled phonon beneath it; thus the bare phonon cannot be observed, in contrast to the case of the depletion layer.

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CHAPTER 1

INTRODUCTION

In the past century the studies of materials have been mainly focused on bulk properties. The understanding of surfaces and fundamental surface related processes has become feasible only in the last 30 years since modern technologies were developed. The role of advanced technologies is two-fold. First, the demand to understand many revolutionary new products, such as semiconductor devices, or fundamental processes, such as catalysis and corrosion, has been the driving force for the tremendous expansion of surface science. Second, only with innovative new surface sensitive techniques developed recently have the studies of atomically clean surfaces become possible.

In surface science, the study of semiconductor surfaces is one of the major efforts. Since the first semiconductor transistor was invented, the device industry has been developing explosively. Not only has the understanding of many fundamental chemical processes become crucial in improving the manufacturing and performance of the device, the device itself has reached such a high level of integration that boundary and interface effects have become important or even dominant in determining the characteristics of performance. Two aspects of the problems have been investigated extensively. One is the electronic and chemical properties of the semiconductor surfaces and interfaces, the other is the electrical behavior near the surface and interface region. These two issues are emphasized in

this thesis.

In many semiconductor devices, the functional behavior is determined mainly by the transport properties of the free carriers in the space charge layer. The electronic spatial distribution and dynamic response are very fundamental problems. The study of these properties can be particularly important in the understanding of the phenomena encountered in devices, superlattices, and layer structure materials where, since the layer can be very thin, the electrons move entirely in the space-charge region. The rapid development of device technology demands extensive research on these issues. From a physical standpoint, the behavior of an electron in the space charge layer is also an interesting problem. The static electron density profile and the dynamic response become complicated when the dimension of the space charge layer is comparable to the electron wavelength. Experimental studies not only provide new information but also stimulate theoretical modeling and calculations.

In this thesis the GaAs(110) surface, which is an example of a depletion-type space charge layer, and the InAs(110) surface, which is an example of an accumulation layer, are studied. The plasma oscillation of the free carriers and the coupling of the plasmon with the optical phonon are observed. We observe the frequency shift and intensity change of the coupled plasmon-phonon modes as the space charge layer forms. An intrinsic electron-depleted region near the surface is observed for the clean surface and even for the surface with a strong accumulation layer.

Plasmons and phonons on the GaAs (110) surface have been studied by several groups. In this thesis, however, the issue is attacked with a different approach. First, because the doping is such that the coupling between plasmon and phonon is strong, three losses are observed. The data reveal details of the spatial distribution

of electrons in the space charge layer and provide excellent experimental data for theoretical calculations. Second, a systematic measurement of the coupled plasmon and phonon is carried out as the space-charge layer forms. The experimental study together with a model calculation provide an effective and reasonably accurate measurement of the band bending.

On most free semiconductor surfaces, only a depletion space-charge layer exists. This is the primary reason that most existing high resolution electron energy loss spectroscopy investigations of space-charge regions focus on the depletion layers. However, accumulation layers play an important role in many phenomena, such as transport phenomena in layered structure devices or sub-band formation. For this reason we studied the InAs(110) surface, because it develops an accumulation layer when exposed to hydrogen. In an accumulation layer, where the electron density varies rapidly in the near surface region, the simple step model employed by many authors to describe depletion layers is not adequate, and a more sophisticated model is needed.

The mechanisms of chemisorption and chemical reaction are basic issues in designing and manufacturing semiconductor devices and various semiconductor gas sensors. Although a huge amount of work has been done, many phenomena are still not clearly understood. In this thesis, hydrogen chemisorption on III-V compound semiconductor (110) cleaved surfaces is selected for study. With primarily the 1s orbital involved in the chemisorption, the H atom is a relatively simple case. A thorough understanding of the system may shed light on studies of other more complicated chemisorption systems. Furthermore, the interaction of hydrogen with semiconductor surfaces is important by itself for the following two reasons. First, hydrogen plasma etching is widely used in the device industry. Second, because of the fact that the residual gas in ultra-high vacuum (UHV) is mainly hydrogen,

research on the effects of H on surfaces provides valuable background data for other studies. HREELS is the ideal tool to study H chemisorption since the vibrational stretch mode is easily observed, while other techniques are much less sensitive to the influence of H atoms. We have measured H chemisorption on the (110) surfaces of GaAs, GaP, InP, GaSb, InSb, and InAs. It is observed that atomic hydrogen adsorbs on both the surface cation and anion atoms via the dangling bonds. A careful H uptake measurement reveals no evidence of preferential adsorption on the anion or cation for the entire exposure range. The effective charge transferred along the H-substrate bond is calculated from the measured stretch intensity and a model based on the electronegativity of the element is proposed to qualitatively interpret the data. The idea that the clean surface relaxation is healed by H adsorption is supported by the analysis. The interaction of H with surfaces after light sputtering is also investigated to serve as a link between the laboratory surface and real-world devices. It is found that the H-anion stretch is generally enhanced, especially for samples containing In. We suggest that the local cation clustering due to sputtering is responsible for the enhancement.

The thesis is organized as follow. After this introduction descriptions of experimental techniques, with the emphasis on HREELS, the vacuum system, and sample preparation are given in Chapter 2. The experimental procedures are also discussed. Chapter 3 reviews the theoretical aspects of HREELS where the purpose is to review the basic idea and appropriate physical models for dealing with the interaction of the probing electron beam with a solid surface, rather than a rigorous general quantum mechanical derivation which can be found in the literature. Then some useful conclusions and results for more complicated systems, which are crucial for data interpretation, are discussed. The studies of coupled plasmon-phonon excitations in the space-charge region of semiconductors are

presented in Chapter 4 for GaAs and Chapter 5 for InAs. Chapter 6 discusses hydrogen chemisorption on the cleavage surfaces and surfaces which were lightly sputtered after cleaving. Chapter 7 is a summary.

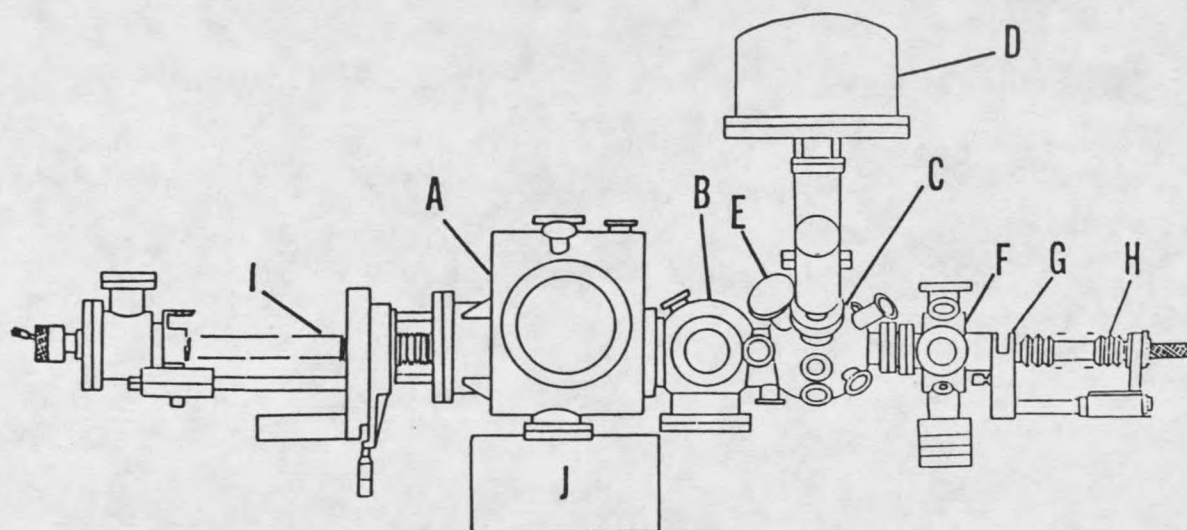
CHAPTER 2

INSTRUMENTATION AND EXPERIMENTAL DETAILS

Instrumental Layout

The experiments were performed with two systems. One is a commercially built Leybold chamber equipped with spectrometers to do high resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED), X-ray photoemission spectroscopy (XPS) and ultra-violet photoemission spectroscopy (UPS). The other system is a home-designed chamber which is in principle similar to the first one; it also contains HREELS, LEED, XPS and UPS. The data acquisition unit of the latter system is more advanced and sophisticated. In this section, the focus will be on the chamber and layout of the first system, and on the data acquisition unit of the second system.

Figure 1 shows the schematics of the experimental chamber. It consists of a sample manipulator, a HREELS chamber, LEED chamber, XPS chamber and the pumping system. The stainless steel chamber is magnetically shielded with thin sheets of material of high magnetic permeability attached to the inside of the chamber. Chamber A contains the Leybold ELS-22 spectrometer. Chamber B contains the Varian (four grids) standard LEED optics for structural study. Chamber C has the X-ray source, ultra-violet light source, ion sputter gun and a single



L-H LOW-ENERGY, ELECTRON-ENERGY-LOSS AND PHOTOELECTRON SPECTROMETERS

- | | |
|--|--|
| A. LEELS Analysis Chamber | E. SIMS Detector |
| B. LEED Analysis Chamber | F. Sample Preparation Chamber |
| C. ESCA, UPS, AES, SIMS Analysis Chamber | G. Fast-Entry Sample Interlock |
| D. ESCA, UPS, AES, ISS Hemispherical Energy Analyzer | H. Hot/Cold Sample Rod |
| | I. x,y,z,θ Hot/Cold Sample Manipulator |
| | J. Main Chamber Ion and Turbomolecular Pump System |

(Ion Sputter Gun and UV Lamp Omitted from Figure)

Fig.1 Schematics of the experimental chamber

channel hemispherical energy analyzer.

The main chamber is pumped by a Leybold 360 l/s turbo pump backed with a mechanical pump, an ion pump and a Ti sublimator together with a liquid nitrogen cold trap. The preparation chamber is pumped by a turbo pump and is isolated from the main chamber by a viton O ring. The preparation chamber is used for quick introduction of samples for XPS without baking and is not used in our experiment. Without baking the system, the best pressure is 10^{-8} torr, which is obviously too high for surface studies where surfaces must be kept clean for hours. The baking temperature is pre-set at 170° and the baking time is usually between 15 and 20 hours. After the baking, all filaments which are to be used in the experiment are degassed near their operating current while the chamber is still hot, so the gas released will be pumped out instead of sticking on the chamber's wall and affecting the ultimate high vacuum. The experimental base vacuum of 1×10^{-10} torr is reached in two to three days.

The data acquisition system consists of a host computer, CAMAC crate, and a data acquisition unit (DAU) which is a computer built into the control unit for the Leybold multichannel energy analyzer used in XPS and UPS. The host computer is an HP 300 series and is interfaced with the CAMAC system and the DAU. The CAMAC crate consists of a controller, a timer scaler and a 16 bit digital to analog converter (DAC). The output of the DAC is connected via an operational amplifier in series with the HREELS ramp control unit to scan the analyzer slit potential. The channeltron signal amplified by a preamplifier, passes through a filter which discriminates the low amplitude noise and outputs TTL pulses to a ratemeter and timer scaler. The counts are then stored in the computer. For the DAU, the host computer only specifies the condition of the scan; the DAU transfers the data to the host computer. Beside controlling the experimental runs, the host computer also

performs data manipulation and hard-copy printing.

High Resolution
Electron Energy Loss Spectroscopy

In these investigations the primary goal of HREELS was to study the vibration of chemisorbed molecules and surface phonon and plasmon modes. These vibrations have typical linewidths of less than 1 meV, while the instrumental resolution of our spectrometer is at best 4 meV obtained with the monochromator beam exiting directly into the analyzer (straight through configuration). For all deflection energy analyzers, the resolution is proportional to the pass energy; thus the pass energy of the HREELS spectrometer must be very small to meet the resolution requirement. In most monochromator designs, the pass energy is less than 1 eV. For such a small pass energy the materials used to construct the spectrometer may not be considered an equipotential surface since its work function variation can produce electric fields, and in addition, the metal surface also can be contaminated by an insulating material and could charge up to several tenths of a volt. All these effects will influence the low energy electron trajectory and greatly degrade the performance of the spectrometer. Since the patch fields due to contamination are uncontrollable, the tuning of the spectrometer is not systematic and reproducible. The problem is lessened but not totally eliminated by coating all surfaces with graphite, a material whose surface properties are quite stable. This variability in the spectrometer surface properties is the primary reason that the potential setting of the spectrometer lenses will be different from day to day or after gas exposure. Thus a good portion of the experimental time is spent on tuning the spectrometer to optimum performance. The other difficulty in high-resolution spectrometer design is the space charge effect which arises from the high beam current density. The

electrons tend to diverge from the beam trajectory due to Coulomb interaction among them, and the effect is enhanced by the low pass energy required. With all these problems, a relatively simple and short lens system is practical, since work function variations will reduce the transmission of a lens system.

Most HREELS spectrometers are based on a pair of 127° cylindrical dispersive elements employing real slits, and coupled to a simple double-plate lens system. This design was developed by Ibach¹ and Froitzheim² and has been proven highly successful. Figure 2 shows a schematic diagram of the spectrometer.

The filament is "V"-shaped with the needle like tip in the repeller region. The repeller is negatively biased to repel the thermionic electrons generated by the filament. The electrons are then focused by three electrodes onto the pre-monochromator's entrance slit. All three lenses are made of two pieces so that they not only focus the electron beam but also deflect the beam. The size of the entrance slit to the monochromator is $0.2\text{mm} \times 6\text{mm}$, and the slit is placed at the main radius of the capacitor, which is defined as the radius with the same potential as the slit. The direction of the slit is along the axis of the cylindrical capacitor. The small slit size is necessary in a high-resolution spectrometer, although it limits the maximum beam current transmitted. After passing the two stages of monochromatization, the beam is accelerated to the primary beam energy and focused on the sample by two thick electrodes, e_1 and e_2 . The opening of the two electrodes is approximately $5\text{mm} \times 20\text{mm}$, which is much larger than the monochromator slit to allow for maximum transmission. These two electrodes are also constructed with two pieces to deflect the beam; e_1 is perpendicular and e_2 is parallel to the incident plane, which is defined as the plane containing the incident beam and the surface normal. The beam reflected from the sample is decelerated and focused onto the analyzer entrance slit. The analyzer is very similar to the

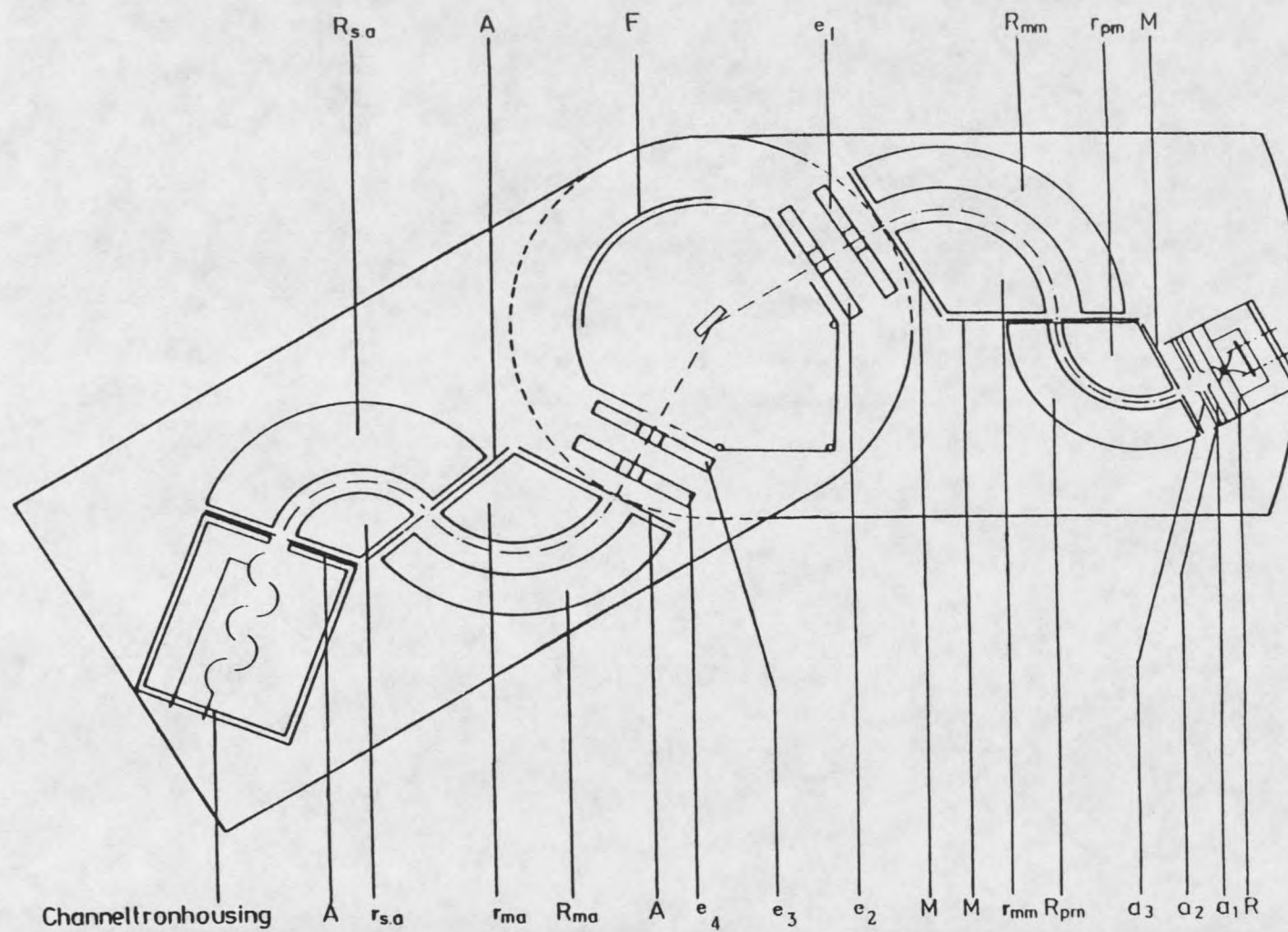


Fig.2 Schematics of 127° cylindrical ELS Spectrometer.

monochromator, except the slit potential is ramped to scan the energy. In this way, the whole spectrum enters the analyzer, but only the electrons with an energy equal to the pass energy will reach the detector.

For such a system, the resolution ΔE can be expressed as

$$\frac{\Delta E}{E_{\text{path}}} \leq K + b\alpha_m^2 + dh^2 \quad (2.1)$$

where K is a geometrical constant dependent on the slit width and the main radius, b is a constant depending on the field angle and α_m is the maximum angular divergence of the entering electrons, d is a constant and h is the mean slit height. In this expression, one sees that the first and third terms are constant once the system is constructed. The angular divergence of the beam described by the second term very often causes poor resolution if the target enlarges the angular distribution of the reflected beam.

In principle, the voltage of each lens can be calculated and pre-set once the pass energy and primary energy are determined. However, such an ideal case is never realized in the actual operation because of the patchy field mentioned earlier. Thus, a lot of time is spent on the tuning of the spectrometer.

To initiate the tuning, a voltage settings which was used before and has a fairly large pass energy is employed. If the current on the sample is larger than 5×10^{-11} A, it suggests that the setting for the monochromator and anodes is good. The sample should be positioned in such a way that the reflected beam is towards the analyzer slit. Often this process will produce some counts in the detector.

Once a satisfactory signal is found on the detector, the effort is then focused on the improvement of resolution and count rate to approach the ultimate

conditions. As mentioned earlier, the resolution is inversely proportional to the pass energy; thus a systematic way of improving resolution is to reduce the pass energy.

In HREELS experiments, it is sometimes necessary to change the primary beam energy, either because a change of probing depth is needed or simply to avoid a low reflectivity at certain primary energies. This is achieved by tuning the potentiometer labelled "primary energy". Obviously, the acceleration and deceleration optics will be changed accordingly. In principle, all other electrode's voltages need not to be adjusted; however, all electrode voltages should be tuned again to restore the optimum setting. This discussion demonstrates again the complexities of high-resolution spectrometers.

Low Energy Electron Diffraction

In our experiments, LEED is supplementary and is used to monitor the surface order, so it is discussed only briefly here. The LEED unit is the commercially available Varian Model 981-0127 optics with power supply.

The principle of the LEED is to utilize the wave nature of electrons to produce a diffraction pattern from the surface. Such a pattern is the replica of the reciprocal lattice of the surface atomic structure. In our experiments, the LEED patterns are visually examined after the cleave, with two or three beam voltages. After the hydrogen exposure, the patterns are examined again for the same beam voltages at precisely the same settings so that the change in background and spot brightness can be compared to those of the cleaved surface. After the hydrogen exposure, some spots may disappear from the pattern of the cleaved surface. These effects are caused by hydrogen induced structural changes in such a way that the

unit cell is preserved but the diffracted beam intensities are changed.

The electron optics consists of four concentric grids and a fluorescent screen. The sample is placed at the target point, which is the spherical center of the grids. The inner grid and the sample are usually at the same potential to ensure a field-free region between sample and grids. The second and third grids are used as suppressor to obtain a sharp and low background pattern. The fourth grid usually is held at ground potential to prevent field penetration by the screen voltage, which is in the keV range. The electron gun unit contains a cathode, a deflection lens and a focusing lens. In operating the system, the deflection lens must be set properly to maximize the gun transmission. This can be done by placing the sample in front of the electron gun and measuring the current between sample and ground.

X-ray and Ultra-violet Photoemission

Photoelectron spectroscopy has been proved very powerful in surface analysis. The primary reason is the short (2-50 Å) escape depth of the photoelectrons with energy ranging from several volts to 1000 volts; thus the probe is extremely surface sensitive. X-ray photoemission spectroscopy (XPS) uses the characteristic X-ray $K\alpha$ emission of Al (or Mg) to excite the core level electrons of the sample. The excited electrons have a specific kinetic energy determined by the photon energy and the core level binding energy. The location of the line produced in the electron energy spectrum can be used for element identification. The intensity of the line reflects the relative concentration of the element measured. The latter property is used in our experiment to monitor the surface stoichiometry. The core line of each element in the compound is measured after cleavage of the crystal, and the same lines are measured again after the surface treatment and compared to those of cleaved

surface. The change of the relative intensity then indicates the change of surface composition.

Ultra violet photoemission spectroscopy (UPS) uses the narrow characteristic line of a noble gas (e.g. He, Ne) discharge glow to study the shallow core line or valence band structures of the sample. The shift of the core line reveals the band bending near semiconductor surface. The discharge is induced by high voltage applied at two ends of a quartz capillary. The UV light generated is led to the UHV chamber by another capillary with an inner diameter of about 1 mm. It is thus necessary to differentially pump the system in two stages. With the two stages of differential pumping the pressure in the UHV chamber then can be maintained at lower 10^{-9} torr range.

Ion Sputtering

An ion sputtering technique is used to disrupt the surface order in our experiment. The principle of ion sputtering is to use energetic noble gas ions, with energies usually on the order of one keV, to bombard the surfaces. These ions collide with the atoms in the near-surface region, thereby transferring energy to the atoms. As a result, the atoms are removed from the surface.

The ion gun used was manufactured by Leybold-Heraeus. Thermal electrons emitted from a filament are accelerated by an anode grid with a potential of 100 V, which is the optimum energy to ionize most gases. The ions generated are then extracted from the source volume by a voltage of about 150 V and are accelerated to the desired energy. A focus lens behind the extractor focuses the ions to a beam diameter of 0.1mm onto an aperture with an opening of 1mm. This small aperture also results in a pressure drop between the ion generation volume and the main

experimental chamber. After passing through the aperture, the beam is focused by two tubular lenses onto the sample's surface. Two pairs of parallel plates perpendicular to each other are placed between the lenses and the sample to deflect the beam. The deflection plates can be supplied with an AC voltage to raster the beam over the desired surface region.

In our experiment, the ion voltage is controlled between 500 and 1000 eV to avoid excessive damage, such as preferential sputtering or macroscopic structure formation. All sputtering is carried out with an electron emission of 3 mA, a rastering area of 8mm×8mm, an argon pressure in the main chamber of about 2×10^{-7} mbar, and a sample current of about 0.2-0.3 μ A; the total ion dose, under 10^{15} over a surface area of 5mm×5mm, is controlled by the sputtering time provided that all ions are singly-ionized.

Sample Preparation and Manipulation

All samples consisted of single crystal bars with a 5mm×5mm cross section and approximately 25mm long. The cleavage surface (the (110) plane) is the cross section of the bar. The crystal bar was first slotted on one side for cleavage convenience. The crystal is then mounted on a sample holder made of oxygen-free copper. A platinum-10% platinum-rhodium thermocouple is pressed between the sample and the holder to measure the sample temperature. The sample holder is mounted on a manipulator which has three translational and two rotational movements. One rotation swings the sample surface normal in the scattering plane defined by the HREELS spectrometer, the other can be used to incorporate an azimuthal rotation around the surface normal or a tilt rotation to move the surface normal perpendicular to the scattering plane. This last degree of freedom was not

used in the experiment. The sample holder is in good thermal contact with a cooling reservoir which can be filled with liquid nitrogen or liquid helium by passing the coolant through two stainless steel tubes connected to the reservoir inlet and outlet. The final temperature was 80 K for one system and 110 K for the other. The discrepancy is due to the difference in thermal conduction between reservoir and sample for the two systems.

Experimental Procedures

In preparation for cleavage all the filaments are degassed and the cleaver is aligned with the crystal. The cleaver consists of a tungsten-carbide blade with a 30° pitch and a flat anvil; the crystal is pressed between the blade and the anvil while the cleavage plane is parallel to the knife side. Precise geometrical alignment is the key to successful cleavage. If the crystal cannot be cleaved with fairly strong pressure, one should check the alignment and do it again. Good cleavage does not need strong force.

Whether doing HREELS, LEED, XPS or hydrogen exposure, the corresponding filament is always degassed before the sample surface is moved in front of the beam to avoid excessive contamination released by the filament. In the case of UPS, in addition to possible outgassing, the very high photon flux during the ignition of the discharge could assist residual gas adsorption on the surface³. Thus, the sample surface should not face the UV light during this period of time.

The hydrogen exposure was made with the sample surface in line of sight of the filament, which is used to dissociate hydrogen molecules. The distance between them is about 5 cm. During exposure the ion pump was turned off and the turbo pump was kept running. The H₂ gas flows into the vacuum chamber through a leak

valve which is capable of controlling the pressure in the low 10^{-9} torr range. The exposure is recorded in Langmiurs ($1 \text{ L} = 1 \times 10^{-6} \text{ torr} \times \text{sec}$). Both the turbo pump and the ion pump are not very efficient in pumping hydrogen, thus the high hydrogen background after a series of exposures on one cleave surface is pumped out by using the Ti sublimator, which is an effective hydrogen pumper.

The clean cleaved surface was characterized with LEED, XPS and UPS when necessary. In the LEED measurement, the pattern was examined visually for three or four different primary energies. The specular (0-0) beam should be found and aligned to the center of the screen; this position is used to define the sample rotation for the HREELS measurements. After ion sputtering or hydrogen exposure, the surface was characterized again with these techniques to monitor the change in surface order, stoichiometry and band bending. Care is taken to place the sample precisely at the same position as in the former measurements.

In HREELS measurements, the sample is moved into the HREELS chamber and placed at the target position as close as possible judged by eye. The most sensitive move usually is the rotation angle which defines the direction of the reflected beam. The procedure described earlier was then carried out: the voltages on all the electrodes, and the sample position, should all be adjusted repeatedly until satisfactory intensity and resolution are obtained. This process is very time consuming for the first cleave, and occasionally contamination of the surface is large enough to prohibit certain measurements on such surface.

Once the optimum setting is found, it can be used for the entire experiment run although small changes are needed after hydrogen chemisorption or even after one day. Large changes of the spectrometer voltage settings are always avoided to maintain constant transmission. Since quantitative measurements were needed, the same HREELS sample position was regained after movement for other procedures.

CHAPTER 3

THEORY OF HREELS

The interaction of probing electrons and solids has been studied for many years. In particular a theory has been developed to describe the physics of electron energy loss spectroscopy.⁴⁻⁷ In this chapter the details and rigorous derivation of the theory will not be reviewed. Instead, we first discuss the physical meaning of the loss function from the view point of classical electrodynamics. Second, we examine the interaction of a probing electron with adsorbed molecules and demonstrate the characteristics of the dipole scattering mechanism. We then discuss the selection rules in the dipole scattering regime. Finally, for the convenience of data interpretation in later chapters, we discuss some important and relevant results of the quantum mechanical calculation of the scattering cross section by Mills and Ibach⁷.

Figure 3 schematically illustrates the high-resolution electron energy loss experiment. A highly monochromatic and well-collimated electron beam with energy of E_I and momentum $\vec{k}_I$ impinges on the solid surface. The solid in this case consists of a thin overlayer and the bulk solid with dielectric functions ϵ_s and ϵ_b , respectively. The scattered electrons of energy E_s and momentum $\vec{k}_s$ are collected by an analyzer. During the scattering process conservation of the total energy and the momentum parallel to the surface requires $E_s = E_I - \hbar\omega$ and $\vec{k}_{s\parallel} = \vec{k}_{I\parallel} - \vec{Q}_{\parallel}$, where the subscript $\parallel$ denotes the component parallel to the surface, and $\hbar\omega$ and $\vec{Q}_{\parallel}$ are

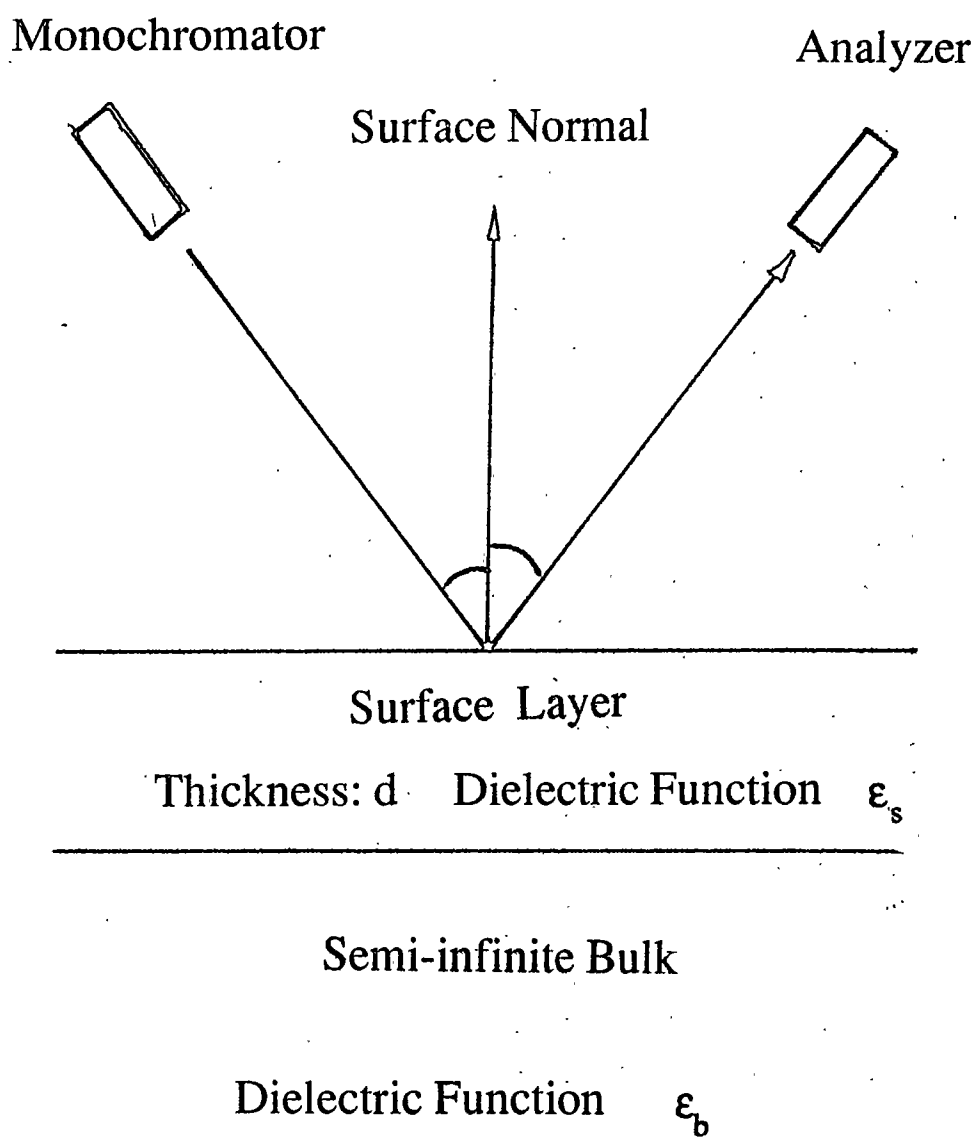


Fig.3 Principle of HREELS

the energy and the momentum, respectively, for the excitation created in the medium. The interaction of the probing electron and the solid usually can be separated into two regimes. One is the so called dipole scattering regime, in which the electrons are scattered by the dipole field generated by charge fluctuation in the solid into a very narrow angular cone with axis along the specular reflected direction; thus the momentum transfer parallel to the surface is very small. The information obtained is closely related to long range correlations of the medium such as the collective excitations of plasmon and phonon. The other regime is the impact scattering regime where the probing electrons are scattered by the local atomic or molecular field. The signature of such interactions is the large momentum transfer parallel to surface, since the electron does not emerge along the specular direction defined by the Bragg diffraction. In this regime the resultant spectra reflect the local properties of the surface such as the electronic and geometric structure of an adatom. The theory to describe this interaction is still developing.^{8,9} As in most HREELS studies, all of our spectra are collected along the specular direction, and thus they will be interpreted within the dipole scattering regime.

One simple model widely used in describing HREELS correlates the scattering cross section of the probing electrons to the dielectric response of the medium as discussed by Froitzheim.¹⁰ Let $\epsilon = \epsilon_1 + i\epsilon_2$ be the dielectric function of the solid. An incoming electron has an accompanying electric field which will polarize the medium. The induced field of the polarization interacts back on the electron and damps its motion; in other words, the energy lost by the probing electron is dissipated by the medium. In the context of this idea, the loss function can be constructed classically. The amplitude of the field in the bulk induced by the probing electron in the vacuum is screened¹¹ by a factor of $1/(\epsilon+1)$, and the

intensity is then reduced by a factor $1/|\epsilon+1|^2$. The energy lost due to the interaction of the electric field with the medium is proportion to ϵ_2 .¹⁰ Thus, the probability for energy loss will be proportional to

$$\text{Loss function} \propto \frac{\epsilon_2}{|\epsilon+1|^2} = \text{Im}\left[\frac{-1}{\epsilon+1}\right] \quad (3.1)$$

where $\text{Im}\frac{-1}{\epsilon+1}$ is the well known surface loss function. A zero in the denominator of the loss function gives a peak in the loss spectrum. Once the dielectric function of the solid is known, the scattering cross section can be calculated with the loss function.

Let us now examine qualitatively how the incoming electron is scattered by a dipole. Following the ideas of Mills and Ibach⁷, we assume that a molecule with a dipole moment p adsorbs on the semiconductor surface. The dipole potential in the vacuum above the surface is

$$V(\vec{r}) = 2pz/r^3 \quad (3.2)$$

where the Z axis is chosen as surface normal and the factor 2 is from the contribution of the image potential. The harmonic time dependence is omitted since it has no effects on the following discussion. The potential in the vacuum must obey Laplace's equation. Thus it is convenient to rewrite Eq. (3.2) as a linear combination of two-dimensional waves with a decaying factor $e^{-Q_{||}z}$ (the surface mode solution of Laplace's equation)

$$V(\vec{r}) = (p/\pi) \int d^2 Q_{\parallel} e^{i\vec{Q}_{\parallel} \cdot \vec{r}_{\parallel}} e^{-Q_{\parallel} z} \quad (3.3)$$

where $\vec{Q}_{\parallel}$ is the two-dimensional wave vector and $\vec{r}_{\parallel}$ is the projection of $\vec{r}$ onto the surface. For a particular $\vec{Q}_{\parallel}$, the potential decays into the vacuum according to $e^{-Q_{\parallel} z}$. An electron approaching the surface with an energy E_I and wave vector $\vec{k}_I$ is scattered to a final state energy $E_S = E_I + \hbar\omega_0$ and wave vector $\vec{k}_S$. Within perturbation theory the scattering cross section is proportional to the squared matrix element $|\langle E_I, \vec{k}_I | V(\vec{r}) | E_S, \vec{k}_S \rangle|^2$. Both the incoming and scattered electron are in plane wave states, thus only the component in $V(\vec{r})$ with $\vec{Q}_{\parallel} = (\vec{k}_S - \vec{k}_I)_{\parallel}$ has a non-vanishing contribution to the matrix element. Since the potential decays into the vacuum according to $e^{-Q_{\parallel} z}$, the range in which the probing electron experiences strong interaction is about $Q_{\parallel}^{-1}$. From this result it follows that the total interaction time is approximately $\Delta t = 2Q_{\parallel}^{-1}/v_0$, where v_0 is the electron velocity and the factor 2 arises because the electron interacts with the dipole both while approaching and leaving the surface. As argued by Mills and Ibach,⁷ if Δt is large compared with the period of the molecule's vibration ω_0^{-1} , the interaction is adiabatic and the electron exits without exciting the mode. On the other hand if Δt is small the interaction time is so short that the probability of exciting the vibrational mode is very small. Consequently for $\Delta t \approx \omega_0^{-1}$ or $\omega_0 \Delta t \approx 1$, the excitation cross section is maximized. With an electron incident normally on the surface $Q_{\parallel}$ is approximately $k_I \theta_S$, where θ_S is the angle between $\vec{k}_S$ and the specular direction. The condition $\omega_0 \Delta t \approx 1$ can then be rewritten as $\omega_0 \Delta t = 2\omega_0 / (k_I v_0 \theta) \approx 1$. Substituting k_I and v_0 with energy E_I , one obtains $\theta_S \approx \hbar\omega_0 / E_I$. Under the usual experimental condition, $\hbar\omega_0 \ll E_I$, and thus θ_S is very small. Accordingly the cross section has a very sharp lobe peaked around the specular direction.

In HREELS, there are also selection rules. For a molecule adsorbed on the

surface, the probing electrons can only interact with those molecules which have non-vanishing normal dipole moment⁷ provided that the static dielectric constant of the substrate is large. This is due to the static induced image charges in the substrate: a parallel dipole will be screened by an opposing image dipole, whereas the normal component of the dipole is enhanced by an image dipole. Thus the absence of a molecular vibration in the spectra only tells one that the molecular dipole normal to the surface is zero; other evidence is needed to prove the absence of the molecules.

For charge fluctuations in the solid, such as plasmons and phonons, the selection rule is that the probing electrons can only interact with the surface mode of the oscillation.⁷ The selection rule arises from the boundary condition. The potential of a charge fluctuation localized at the surface satisfies Laplace's equation $\nabla^2\phi=0$. The surface mode solution is

$$\phi=e^{i\vec{Q}\cdot\vec{r}_{\parallel}}e^{+Qz} \quad (3.4)$$

inside the solid where $z<0$, and

$$\phi=e^{i\vec{Q}\cdot\vec{r}_{\parallel}}e^{-Qz} \quad (3.5)$$

in the vacuum where $z>0$. This field will scatter the probing electron. However, when the fluctuation is a bulk mode, the potential is $\phi=e^{i\vec{Q}\cdot\vec{r}}$. Now, the electric displacement vector $\vec{D}$ also obeys $\nabla\cdot\vec{D}=0$. Since $\vec{D}=\epsilon\vec{E}$, one sees that the dielectric function must be zero for the bulk modes, and so the electric displacement vector $\vec{D}$ vanishes inside the solid. The continuity of $\vec{D}$ at the boundary requires the normal electric field outside the solid to be zero also. Therefore the bulk mode

does not interact with probing electrons in the dipole approximation.

The potential given in Eq. (3.5) can be used in perturbation theory to calculate the scattering cross-section. In practice it is convenient to divide the crystal into two parts as shown in Figure 3. One is the substrate with dielectric constant $\epsilon_b(\omega)$ which may account for the phonon or plasmon excitations. The other is an overlayer with dielectric response $\epsilon_s(\omega)$ and thickness d , which can be thought of as a layer of absorbed atoms or molecules or a layer with different properties than the substrate, such as the space charge layer of a semiconductor. For this system, Mills and Ibach⁷ have shown that the dielectric function used in Eq. (3.1) can be replaced by an effective dielectric function $\tilde{\epsilon}$

$$\tilde{\epsilon}(Q_{\parallel}, \omega) = \epsilon_s(\omega) [1 + \Delta(\omega) e^{-2Q_{\parallel}d}] / [1 - \Delta(\omega) e^{-2Q_{\parallel}d}] \quad (3.6)$$

where $\Delta(\omega) = [\epsilon_b(\omega) - \epsilon_s(\omega)] / [\epsilon_b(\omega) + \epsilon_s(\omega)]$, and the scattering cross section then can be written as

$$\frac{d^2S}{d\Omega(\hat{k}) d\hbar\omega} = |R_I|^2 F(\theta_I, \vec{k}_I; \hbar\omega, \Omega(\hat{k}_S)) \text{Im} \left\{ \frac{-1}{1 + \tilde{\epsilon}(Q_{\parallel}, \omega)} \right\} \quad (3.7)$$

where θ_I is the angle of incidence, R_I is the reflectance, $\hbar\omega$ is the energy loss, and the function F is a kinematic factor depending on the primary beam parameters and the scattering geometry. This factor determines the sharp dipole scattering lobe and thus the characteristic $\vec{Q}_{\parallel}$ transfer as discussed earlier. The quantitative calculations done in this thesis are based on Eq. (3.7), where a predicted loss structures is obtained by integrating over the solid angle.

Two examples of application, which will be used in later chapters for data

interpretation, are discussed here. First, let us consider the plasmon excitation due to the free carriers in a semiconductor. Suppose the charge density is a constant n_0 up to the surface, so that the overlayer thickness is zero. The dielectric function ϵ_b is then⁷

$$\epsilon_b(\omega) = \epsilon_\infty - \omega_p^2 / [\omega^2 + i\omega\Gamma] \quad (3.8)$$

where $\omega_p^2 = 4\pi n e^2 / m^*$ is the plasma frequency of the carriers, Γ is the damping term related to the mobility, m^* is the effective mass of the carriers and ϵ_∞ is the background dielectric constant. Following Mills and Ibach, the loss function in Eq. (3.7) is derived as⁷

$$\text{Im}\left[\frac{-1}{1 + \epsilon_b(\omega)}\right] = \frac{\omega \omega_{sp}^2 \Gamma}{(1 + \epsilon_\infty)[(\omega_{sp}^2 - \omega^2)^2 + \omega^2 \Gamma^2]} \quad (3.9)$$

where $\omega_{sp} = \omega_p / (1 + \epsilon_\infty)^{1/2}$. We see that the maximum in the loss function occurs at $\omega = \omega_{sp}$. This result will be used to explain the loss structure in the spectra discussed in Chapters 4 and 5.

The second example is the system of uniformly absorbed molecules on the substrate. The dielectric function of this layer of adsorbed molecules can be described by⁷

$$\epsilon_s(\omega) = 1 + \omega_p^2 / [\omega_T^2 - \omega^2 - i\gamma\omega] \quad (3.10)$$

where $\omega_p^2 = 4\pi(e^*)^2 n / M_r$, ω_T is the vibrational frequency of the adsorbed molecules, n is the density of the molecules, e^* is the effective charge, γ is the reciprocal

lifetime of the excitation, and M_r is the reduced mass. The thickness of the overlayer is only a few Å, and thus $Q_{||}d$ is much smaller than 1. The loss function in Eq. (3.7) can be approximated as⁷

$$\text{Im}\left(\frac{-1}{\tilde{\epsilon}+1}\right) = \text{Im}\left(\frac{-1}{\epsilon_b+1}\right) + \text{Im}\left(\frac{-Q_{||}d}{\epsilon_s}\right). \quad (3.11)$$

The first term in Eq. (3.11) is the substrate loss function and the second term is the surface loss function which accounts for the effect of adsorbed molecules. The second term can be further written as

$$\text{Im}\left(\frac{-Q_{||}d}{\epsilon_s}\right) = \frac{Q_{||}d\gamma\omega\omega_p^2}{(\omega^2 - \omega_T^2 - \omega_p^2)^2 + \gamma^2\omega^2}. \quad (3.12)$$

The maximum in the loss function occurs at the frequency $\omega_s^2 = \omega_T^2 + \omega_p^2$. To compare with the measured loss peak intensity, one needs to integrate the scattering cross section Eq. (3.7) with the loss function in the form of Eq. (3.12). Mills and Ibach have calculated the cross section in Ref. 7 as

$$\frac{I_{\text{inel}}}{I_{\text{el}}} = \frac{S}{|R_I|^2} = \frac{2\pi\hbar}{a_0 E_I \cos\theta_I} (1 - 2\vartheta_E)^{1/2} F_S(\hat{\vartheta}_C) \frac{e^{*2} n_s}{M_r \omega_s \epsilon_\infty^2} \quad (3.13)$$

where $n_s = nd$ is the areal density of the adsorbates and ω_s is the measured frequency of the molecules, a_0 is the Bohr radius, $\vartheta_E = \hbar\omega_s/(2E_I)$, and $\hat{\vartheta}_C = \vartheta_C/\vartheta_E$ with ϑ_C as the analyzer acceptance angle, and $F_S(\hat{\vartheta}_C)$ is⁷

$$F_S(\hat{\vartheta}_C) = [(\sin^2\theta_I - 2\cos^2\theta_I)\hat{\vartheta}_C^2/(1+\hat{\vartheta}_C^2)] + (1+\cos^2\theta_I)\ln(1+\hat{\vartheta}_C^2). \quad (3.14)$$

Eq. (3.13) allows one to calculate the effective charge of an adsorbate from the experimental peak intensity.

In the following chapters the ideas, models and results presented above will be used and discussed in detail to interpret the experimental spectra.

CHAPTER 4

PLASMON AND PHONON MODES IN DEPLETION LAYERS

Introduction

Semiconductors, generally doped intentionally, contain free charge carriers. Control of the carrier density and density profiles at interfaces is what enables the semiconductors to be used as devices. Many transport properties of semiconductors are also determined by these free carriers. Studies of these carriers then provide a foundation for characterizing and improving semiconductor devices.

The primary goal of this investigation is to exploit the surface sensitivity of high resolution electron energy loss spectroscopy to understand the behavior of free carriers in the near surface region. By observing the free carrier plasmon and its coupling with the optical phonon, which is an intrinsic property of compound semiconductors, we are able to investigate the charge distribution in the space charge layer and the interaction between plasmons and phonons. HREELS is uniquely suited for such studies.

Samples with two doping concentrations were used. For heavily doped samples the plasmon line was well above the phonon so plasmon energy shifts caused by changes in the space charge layer could be observed. For the second sample with intermediate doping the plasmon energy was very close to the phonon energy,

producing strong coupling. Using very high resolution three losses were observed for the first time with the method. The data obtained in the two cases were successfully modeled.

Impurity Dopants in semiconductors act either as donors, which can be ionized resulting in free electrons in the conduction band, or acceptors which receive electrons, creating free holes in the valence band. The impurity energy level is slightly below the conduction band minimum for a donor and slightly above the valence band maximum for an acceptor. The actual energy position can be estimated with a hydrogenic model of the electron (hole) for a donor (acceptor). Since the dielectric constant is large (on the order of 10 for most semiconductors) and the effective mass is small ($\approx 0.1 m_e$), the impurity level of a donor is within 5-10 meV of the band edge. At room temperature a substantial number of electrons are excited into the conduction band as free carriers. The exact percentage of impurity electrons thermally excited into the conduction band can be calculated with Fermi-Dirac statistics provided that the impurity energy levels are known.

For most of the doped GaAs crystals the doping level is so high that the hydrogenic orbitals of adjacent impurities overlap. As a consequence the impurity band is formed which intersects with the conduction band. In addition the screening action of the conduction electrons reduces the electron's binding energy around the impurity.¹² Thus for the samples we used, whose doping level is about $10^{18}/\text{cm}^3$, complete ionization is assumed.

Besides the plasmon oscillation due to free carriers GaAs has an eigenmode of lattice vibration known as the Fuchs-Kliwer phonon.¹³ The energy of this optical phonon, 36 meV, is close to the plasmon energy when the free electron concentration is about $10^{18}/\text{cm}^3$. The two eigenmodes are basically charge fluctuations, and generate an electric field outside the crystal. As reviewed in

Chapter 3, the electron beam in HREELS becomes an ideal method to excite these modes. The excitation of the plasmon and phonon will appear in the HREELS spectrum as loss peaks. The energy positions and the intensities of these losses depend on the free carrier density profile.

Matz and Lüth were the first to study the surface plasmon and phonon modes of GaAs(110) by means of HREELS.¹⁴ Two modes were observed, one near 36 meV, mostly phonon-like, and the other, near 20 meV, mostly plasmon-like. The free carrier concentration in their sample was about $3 \times 10^{17}/\text{cm}^3$. Shifts of the two modes were seen as the depletion layer formed. Theoretical calculations were performed later by Egri *et al.* to interpret the spectra.¹⁵ In the experiment, the energy positions of the two modes were measured for two different doping levels on the clean surface and also on the surface after hydrogen exposure, which causes depletion layer formation. However, a systematic study of the dependence of the plasmon on the formation of the space charge layer was not possible because of relatively poor resolution (13 meV) and a small plasmon energy, which placed the loss peak within the large background near the elastic peak.

To study these effects in more detail a crystal (sample A) with very high doping ($\approx 4 \times 10^{18}/\text{cm}^3$) was chosen with its plasmon at about 80 meV, well above the Fuchs-Kliwer phonon. Thus the shift of the plasmon peak could be studied as the depletion layer was formed.¹⁶ The second sample (sample B) had an intermediate doping level of $1.3 \times 10^{18}/\text{cm}^3$, placing its plasmon energy very close to the Fuchs-Kliwer phonon. The result is a strong coupling between the plasmon and the phonon. With very high resolution (≈ 5 meV), three modes were first observed on this sample by means of HREELS.¹⁷

Sample A: Heavy doping

We first examine the case of the heavily doped crystal. The crystal is Si doped n-type GaAs with bulk carrier concentration of $4.07 \times 10^{18}/\text{cm}^3$, determined from infrared measurement of the plasmon absorption edge.¹⁸

The loss spectrum obtained for the cleaved face shows two very strong peaks as illustrated in Figure 4. The primary beam energy is 20 eV and the specular losses are measured at 60° with respect to the surface normal. The peak at 36 meV is readily identified as the previously reported Fuchs-Kliwer optical phonon.¹⁴ The strong peak at the higher loss energy is due to the free carrier plasmon. The position of this plasmon loss depends on the time elapsed after cleaving; the shift is attributed to the modification of the band bending by residual gas adsorption. Thirty-five minutes after cleaving, the plasmon peak is at 80 meV (spectrum not shown here), and at 80 minutes it is at 78.5 meV (the spectrum labeled "cleave" in Figure 1). Assuming the time dependence to be linear and extrapolating back to the moment of cleavage, one would obtain an initial peak position of 81.2 meV. The assumption of the linearity and related implications will be discussed later.

The effects found in the data shown in Figure 4 are the result of depletion layer formation caused by exposure to atomic hydrogen. The exposure level is quoted in terms of molecular H in the presence of a hot W filament since the atomic H flux at the sample is not known. The exposure started at 0.5 L, and continued until saturation occurred. During this process, the plasmon peak continuously shifted down in energy to a final value of 69.8 meV. Along with this shift, the intensity of the plasmon decreased while that of the phonon increased. No shift was observed in the position of optical phonon line.

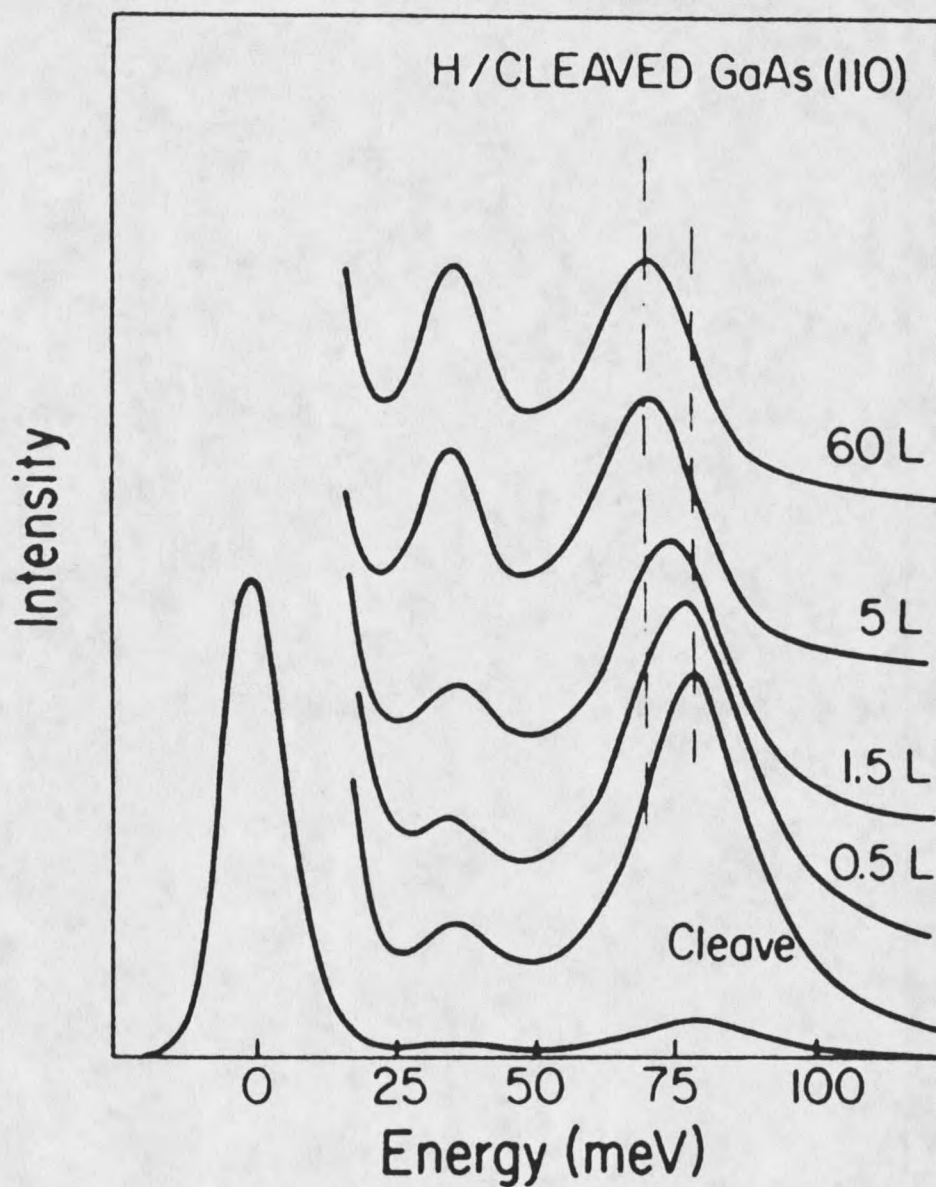


Fig.4

The HREELS spectra of the clean cleaved surface and those after H adsorption are shown. The sample is n-type GaAs doped at $4.07 \times 10^{18}/\text{cm}^3$. The primary energy is 20 eV and the specular loss is measured at an angle of incidence of 60 degrees.

To analyze the data, we begin with a discussion of space charge layer formation and Fermi level pinning. On the clean surface of GaAs(110), the bands are flat up to the surface as illustrated in part a) of Figure 5. There are no intrinsic surface states in the band gap since surface reconstruction "pushes" the states out of the gap.¹⁹ When the surface is exposed to atomic hydrogen, the chemisorption induced defect states²⁰ or hydrogen related surface states can be in the gap. These acceptor-type states are below the bulk Fermi-level, so the conduction band electrons will fill the states. With sufficient density (one percent of the surface atomic density), the surface states will pin the Fermi level at their energy position as illustrated by part b) in Figure 5. The transfer of conduction-band electrons to the surface results in a potential build-up near the surface balanced by ionized donors forming the space charge region. Such a potential depletes the electrons from the space charge layer. The electron density profile in the depletion layer can be modeled classically by solving Poisson's equation.²¹ This approach is simple and straightforward, and quantitative results can be obtained. The assumption implied in this approach is the Thomas-Fermi approximation in which the electric potential is a slow varying function on the scale of the wavelength of the electrons. This local theory breaks down for a high density electron system²². Then a quantum mechanics treatment is needed, where Poisson's equation and the Schrödinger equation are solved self-consistently to obtain the charge density profile.^{22,23} In spite of such limits, a very simple and widely used model for describing plasmons in semiconductor space charge layers is the two-layer model.^{14,16,24-28} In applying the model, the depletion layer is taken as an overlayer with thickness d and no free electrons. Beneath this overlayer is the substrate with bulk electron density determined by the doping (see part (b) in Figure 5). The theoretical description of the two-layer model has been presented in chapter 3. The loss function can be calculated in a straightforward manner which yields very good results. We will use the model in

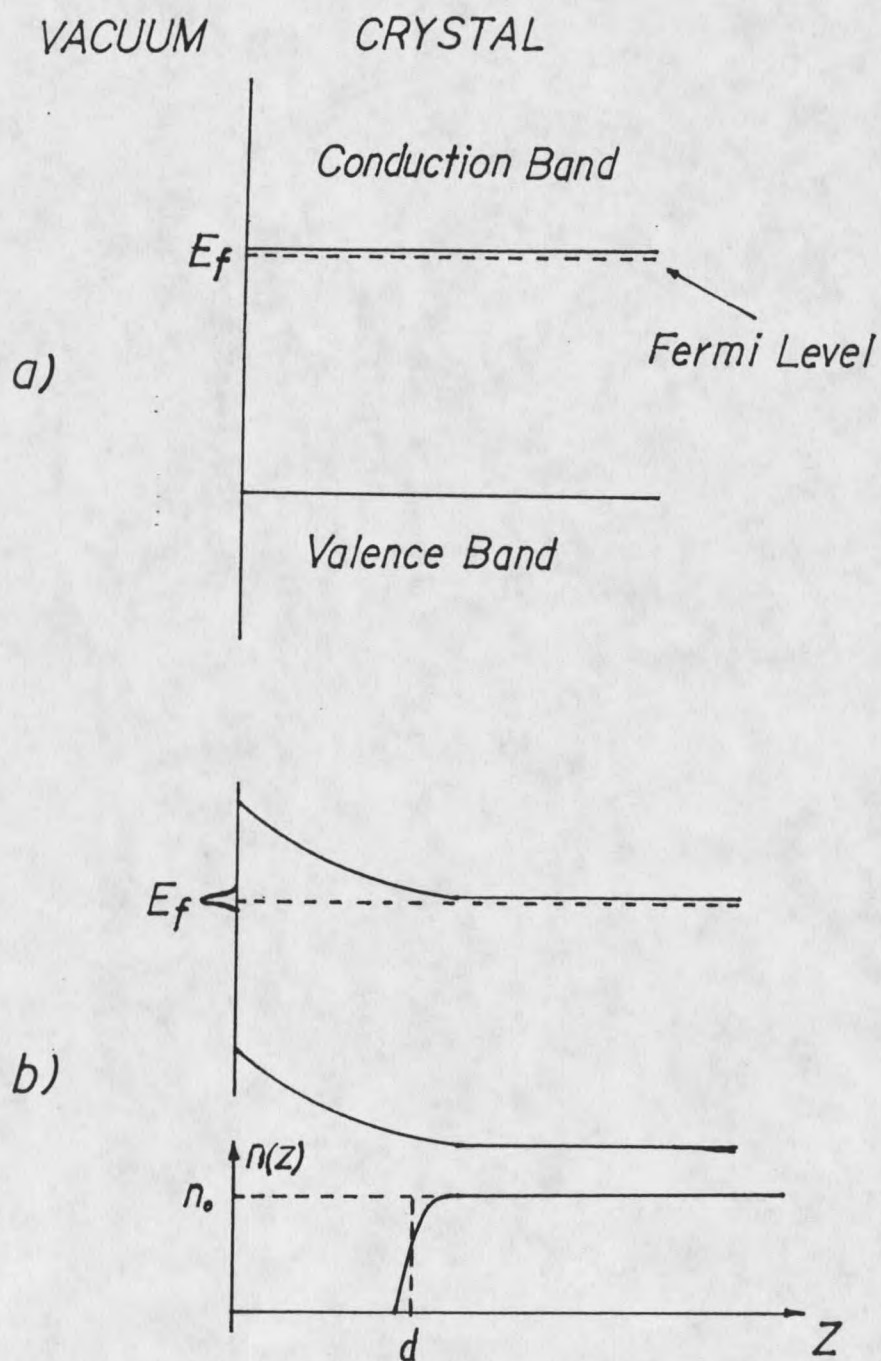


Fig.5 The conduction-band edge of the clean surface (a) and the H chemisorbed surface (b)

interpreting the data.

In the Drude model²⁹ the plasmon energy is

$$\omega_p^2 = 4\pi n e^2 / m^* \quad (4.1)$$

where n is the free electron concentration, e is the electron charge, and $m^* = 0.068 m_e$ is the effective mass of the conduction band electrons and m_e is the mass of a free electron. The surface mode frequency is given by

$$\omega_s^2 = \frac{4\pi n e^2}{m^* (1 + \epsilon(\infty))} \quad (4.2)$$

where $\epsilon(\infty)$ is the high frequency limit of the dielectric constant which for a semiconductor is largely due to the polarizability of the charge cloud of valence electrons. With a free carrier concentration of $4.07 \times 10^{18} / \text{cm}^3$, one evaluates the surface plasmon energy from Eq. (4.2) to be 83 meV. The value is very close to the plasmon energy of 81.5 meV obtained by extrapolating the first measurement back to the moment of cleavage; thus it is confirmed that the loss is really due to the plasmon. Note that the calculated plasmon energy of 83 meV based on the flat band limit is close to the plasmon energy of a fresh-cleave surface. One may infer that the bands are flat for a fresh-cleaved surface. Nonetheless the plasmon energy is about 2 meV lower than predicted; this is attributed to quantum mechanical effects.^{16,22} The physical idea of this effect is that the surface barrier (electron affinity) in GaAs is several electron volts, which is very high compared with the kinetic energy of the conduction band electrons. Thus the electron wave function decays almost to zero at the surface. Since the thermal wavelength of conduction band electron is very long, the requirement of a

vanishing wave function at the surface yields a low electron density region near the surface. The existence of the intrinsic electron depleted region will lower the plasmon energy. However, the conclusion is qualitative and only the direction of the shift is meaningful. The quantum mechanical effect is more manifest for sample B to be discussed later.

A qualitative understanding of the plasmon and phonon losses shown in Figure 4 can be gained from the following consideration. Both the surface phonon and surface plasmon modes establish dipole fields which interact with the probing electron beam producing the peaks in the loss spectrum. Two effects result from the coupling between the plasmon and phonon. First, the phonon intensity is damped by the screening of the electrons. To understand the screening effect, let us examine the case of high electron densities where the plasmon frequency ω_p is much larger than the frequency range studied. The contribution of these electrons to the dielectric function is $-\omega_p^2/\omega^2$. The total dielectric function now is $\epsilon = \epsilon(\infty) - \omega_p^2/\omega^2$. Since $\omega_p > \omega$, ϵ is very large. The boundary condition requires that the electric potential inside the crystal is a factor ϵ smaller than that outside, which means the field of the probing electron is screened by the free carriers. The damping effect was demonstrated clearly by Matz and Lüth where two samples were examined: in the undoped sample the phonon was very strong; in the highly doped sample the phonon was weak.¹⁴ A second effect of plasmon-phonon coupling is the shift of both loss structures. The shifts are small unless the lines are close together, which is observed in our results for the intermediately-doped sample B to be discussed later. In the case of the heavily-doped sample, the plasmon energy is quite high, so the shift due to coupling is not very important. The shift of the plasmon peak position as a function of hydrogen exposure is ascribed to a change in depletion layer thickness. On a surface with a fairly thick depletion layer, the plasmon mode sensitive to HREELS is localized at the interface between the depletion layer and the

bulk. The background dielectric constant $\epsilon(\infty)$ in the depletion layer is quite large (10.9 for GaAs), thus the eigen-mode with which the plasmon oscillates is strongly affected by $\epsilon(\infty)$ and the thickness of the depletion layer. To demonstrate the effect, let us assume two semi-infinite media in contact with each other. The dielectric constant on the left side is ϵ_L and that on the right side is $\epsilon(\infty)$. If free electrons exist in the right side, the dielectric function for the right side is then

$$\epsilon_R = \epsilon(\infty) - \omega_p^2 / \omega^2. \quad (4.3)$$

Since there is no external charge on either side, the electric potential must obey Laplace's equation and so it is given by

$$\phi = A \exp(\vec{Q}_{\parallel} \cdot \vec{r}_{\parallel}) \exp(-Q_{\parallel} z) \quad (4.4)$$

for $z > 0$ (left side), and

$$\phi = B \exp(\vec{Q}_{\parallel} \cdot \vec{r}_{\parallel}) \exp(+Q_{\parallel} z) \quad (4.5)$$

for $z < 0$ (right side). The continuity requirement of the field at the interface gives a secular equation

$$\epsilon_R + \epsilon_L = 0 \quad (4.6)$$

Substituting ϵ_R with Eq. (4.3) and solving for ω , one obtains the frequency of the plasmon eigenmode

$$\omega = \frac{\omega_p}{\sqrt{\epsilon(\infty) + \epsilon_1}} \quad (4.7)$$

If the left side is vacuum, $\epsilon_L = 1$ and the plasmon frequency is that discussed in Eq. (4.2). If $\epsilon_L = \epsilon(\infty)$, it represents an infinitely thick depletion layer, and the plasmon frequency is then $\omega_p / \sqrt{2\epsilon(\infty)}$. We see it shifts down by almost a factor of $\sqrt{2}$ compared to the vacuum semiconductor interface. For a finite depletion layer thickness, the frequency of the plasmon is between the two. Thus as the depletion layer forms due to hydrogen exposure, the plasmon energy will shift down.

The increase of the amplitude of the phonon loss peak as hydrogen is adsorbed is due to the increase of the depletion layer thickness. The effect is due to the nature of the HREELS measurement. As discussed in Chapter 3, the probing depth is limited by the finite values of the momentum transfer $Q_{||}$ and is only about 250 Å in these experiments. As the depletion layer thickness increases, a larger portion of the phonons are unscreened, making a stronger contribution to the loss spectrum. In contrast to the phonon, the intensity of the plasmon decreases as the depletion layer builds up. The plasmon is localized at the interface of the depletion layer; thus as the depletion layer broadens, the plasmon loss weakens.

Theoretical Model for Sample A

For a more quantitative analysis of the behavior of the losses for the heavily doped crystal shown in Figure 4, a model calculation was performed. The model is based on the two-layer model in which the electron charge density profile is approximated by a step function as illustrated in part b) of Figure 5. In this model the dielectric function in the depletion layer has only the phonon contribution⁷

added to $\epsilon(\infty)$:

$$\epsilon_s(\omega) = \epsilon(\infty) - \frac{[\epsilon(0) - \epsilon(\infty)]\omega_{TO}^2}{\omega^2 - \omega_{TO}^2} \quad (4.8)$$

where ω_{TO} is the transverse-optical phonon frequency. Beneath the depletion layer (substrate) both the phonon and plasmon contribute to the dielectric function:

$$\epsilon_b(\omega) = \epsilon_s(\omega) - \frac{\omega_p^2}{\omega^2} \quad (4.9)$$

where ω_p^2 is described by Eq. (4.1). By integrating the cross section (Eq. (3.7)) over the allowed angular acceptance of the analyzer, one obtains the scattering amplitude. For this data set, only the plasmon peak position is calculated with depletion thickness d as an adjustable parameter. The calculated correlation of the plasmon energy with the depletion layer thickness is shown in Figure 6.

The basic result of this analysis is the determination of space charge parameters from the plasmon peak position. To make this determination, the plasmon energy of each spectrum is measured and used to infer the depletion layer thickness from the functional relationship shown in Figure 6.

Using a step function charge density profile and Poisson's equation,²⁹ we obtain the band bending value V_s for GaAs from the equation

$$V_s = 9.1 \times 10^{-23} \frac{n}{\epsilon(0)} d^2 \quad (4.10)$$

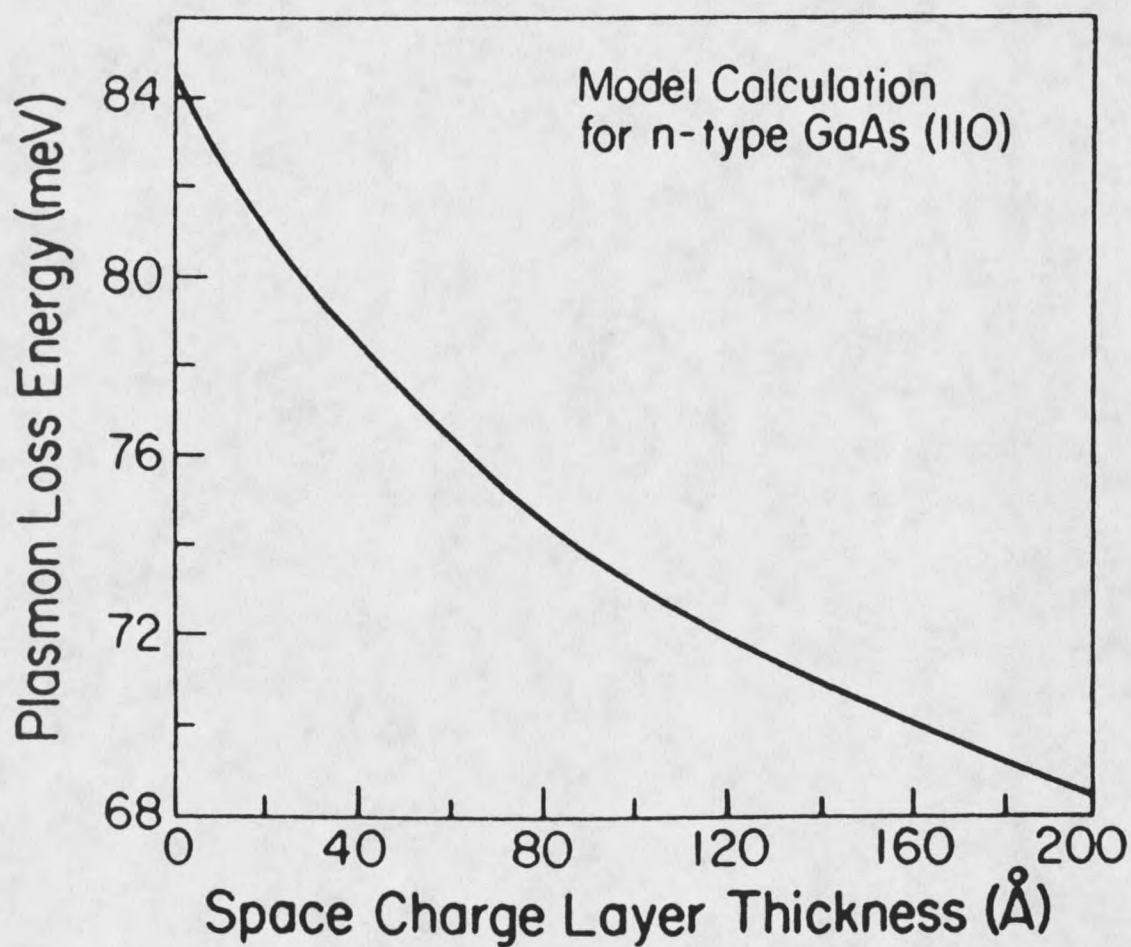


Fig.6

The calculated relation between the depletion layer thickness and the plasmon loss energy is shown for a two-layer model.

where V_g is in units of volts, and $\epsilon(0)$ is the lower frequency limit of the background dielectric function. Table 1 summarizes the experimental plasmon loss peak position, calculated overlayer thickness and band bending as a function of hydrogen exposure. In the table one first notices that the final band bending is 0.71 eV, which is about 0.16 eV higher than the value reported by Bartels et al.³⁰ Secondly, for small hydrogen exposures, namely below 5 L, the increase of overlayer thickness is linearly related to exposure. This is not surprising since the depletion layer thickness is directly proportional to the surface charge in the model, hence the number of surface states is proportional to the H exposure. This is also the physical basis of the earlier assumption that the plasmon energy is linearly dependent on time elapsed after cleaving, because of residual-gas adsorption. Note that such a relation is not guaranteed by the model used for the loss function calculation, and therefore such a linearity proves that a very simple model can give reasonable results.

Table 1 Summary of experimental plasmon peak position (meV), calculated overlayer thickness (Å) and band bending (eV) versus hydrogen exposure (L)

Hydrogen Exposure	0	0.5	1.5	3	5	8	30	60	120
Plasmon Loss Energy	78.5	77.5	74.8	71.8	71.3	71.0	70.5	70.0	70.2
Overlayer Thickness	40	50	78	120	132	139	150	160	156
Band Bending	0.046	0.071	0.17	0.41	0.50	0.55	0.64	0.73	0.69

Sample B: Intermediate doping

The intermediately doped sample has a carrier concentration of $1.3 \times 10^{18}/\text{cm}^3$, measured by the crystal grower (Laser Diode In.) using the Van der Pauw method.. Figure 7 shows a typical HREELS spectrum obtained from the surface of this crystal after hydrogen exposure. The full width at half maximum (FWHM) is about 5.5 meV, which is believed to be close to the instrumental resolution. The structures are more complex than that of the first sample. On the loss side three peaks are present, at 27.6, 36.2 and 43.1 meV. The 36.2 meV loss is due to the unscreened phonon in the depletion layer as discussed earlier, and the other two are the coupled plasmon and phonon localized at the interface between the depletion layer and the bulk. Two modes rather than one mode (as for first sample) are present because a) the uncoupled plasmon energy is very close to the phonon energy thus leading to strong coupling, and b) very high resolution was achieved. The details of these losses will be discussed later in the context of a model calculation. On the gain side, the corresponding gain peaks of these coupled modes can also be seen. Moreover, an additional peak at 15.9 meV is observed which has not been previously reported. The later observation is discussed later.

As done for the heavily doped crystal, spectra for different sample conditions were also taken for the intermediately doped crystal and the results are shown in Figure 8 as solid lines. Spectrum a) which was taken 5 minutes after cleaving has three features at 27.7, 36.9 and 43.7 meV. The peak in the middle only appears as a shoulder. After the UPS spectrum was taken (35 minutes after cleaving) the loss spectrum changed significantly and is shown as curve b). The center peak grew stronger whereas the lower energy peak shifted down about 1 meV, and the higher

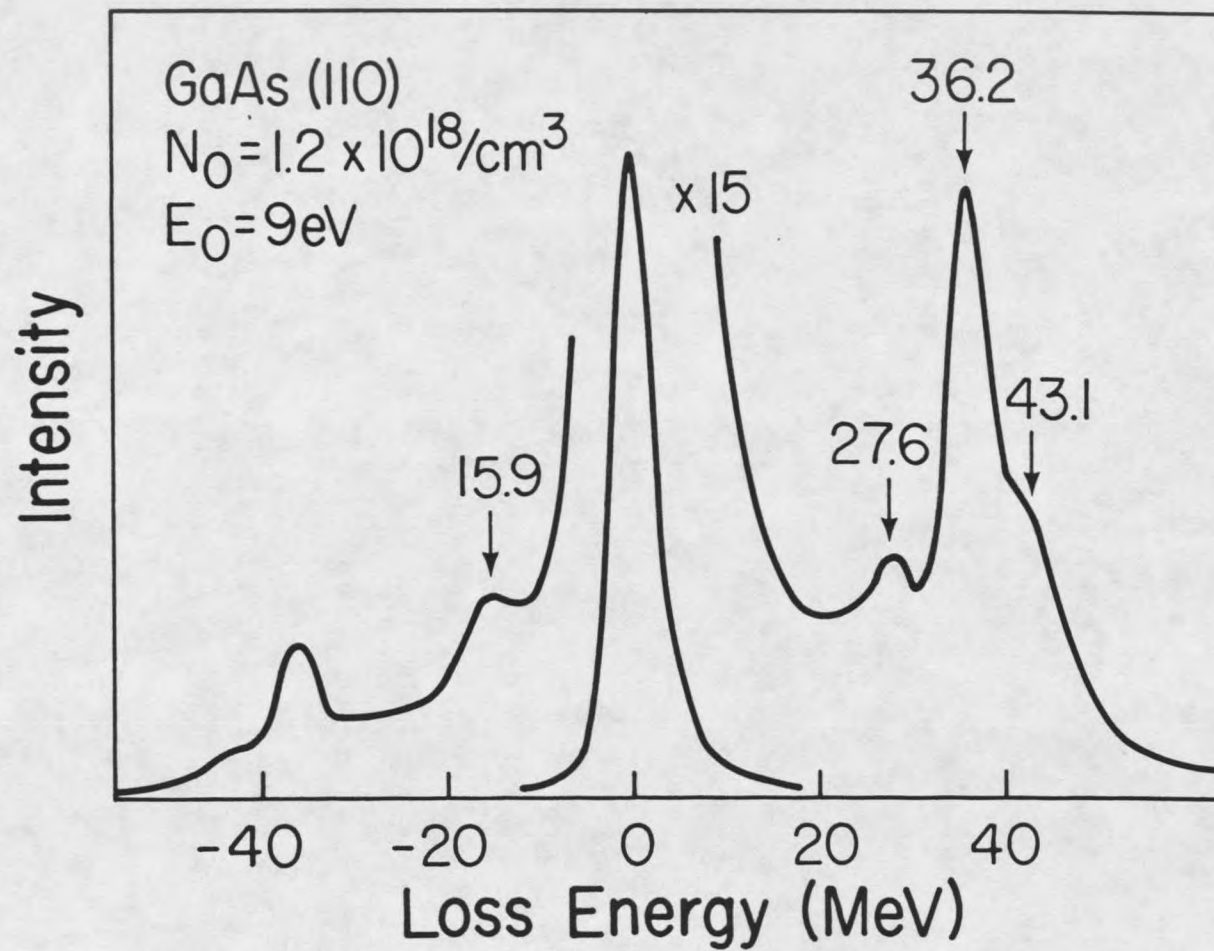


Fig.7

Typical HREELS spectrum of n-type GaAs(110) after hydrogen exposure (500 L). The primary energy is 9 eV and the angle of incidence is 45°

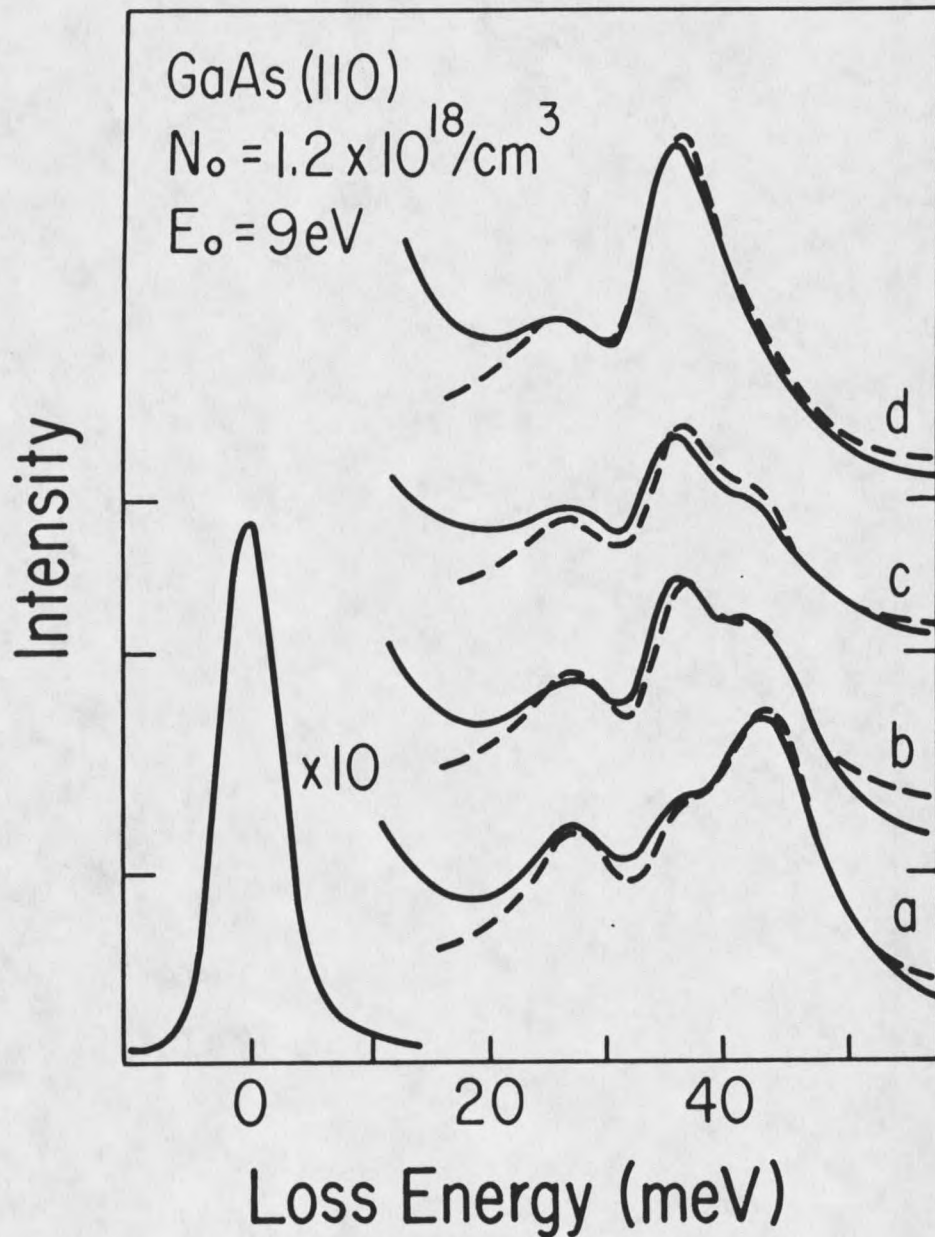


Fig.8

The HREELS spectra for cleaved GaAs(110) surfaces. a) 5 minutes after cleave; b) 35 minutes after cleave; c) 45 minutes after cleave; d) 500 L hydrogen exposure. The dashed lines are the theoretical predictions with $1.2 \times 10^{18} / \text{cm}^3$ as the bulk carrier concentration. The depletion layer thickness used for each spectrum is 110 Å, 180 Å, 200 Å and 260 Å, respectively. The probing electron beam impinged on the surface with 45° incident angle and 9 eV primary energy.

energy peak also shifted down 1 meV with a reduction in its intensity. The spectrum labeled c) was taken 45 minutes after cleaving and its spectral features showed the same kind of change. After 500 L hydrogen exposure the shifts of the spectral features reached their final configuration (see curve d in Figure 8). The first peak is at 26.5 meV, while the second peak at 36 meV has become dominant, and the third peak is only a small shoulder. After the H exposure the UPS spectrum was obtained and used to determine a total band banding value of 0.42 eV. As discussed for sample A the dramatic change of the spectrum as time elapsed is attributed to the residual-gas surface interaction. The species which interacts with the surface cannot be identified at this time.

As argued for the results from crystal A, the qualitative features of the spectra in Figure 8 can be understood in terms of depletion layer formation. In the depletion layer the optical phonon is unperturbed and oscillates without coupling with the plasmon because of the absence of free carriers in the region, so the phonon energy is 36 meV. The thickness of the layer determines the volume of the crystal in which this mode can be excited without free carrier damping and therefore determines the intensity of the bare phonon. One sees that its intensity increases as the depletion layer widens. Below the depletion layer, the phonon couples strongly to the plasmon and this coupling results in two new modes. The energies and the intensities of these two modes not only depend on the electron concentration in the bulk, but also on the environment, namely, the boundary condition as discussed in Eq. (4.4)-(4.7). Different depletion profiles produce different plasmon-phonon mode energies. As a consequence, the loss features are sensitive, in energy position, intensity and line shape, to the details of the space charge distribution.

The most interesting feature in our spectra is the presence of the unscreened

phonon at 36 meV even for the fresh cleaved surface. The reproducibility of this feature for many cleaves rules out the possible explanation of initial band banding due to bad cleaves. Furthermore, to minimize the effect of the depletion layer induced by residual-gas adsorption, the first spectrum was taken within 5 minutes of the cleavage. Thus, the data provide definite evidence for the existence of an intrinsic electron-free region near the surface without the need of any sophisticated model calculation.

As discussed in Chapter 3, the momentum transfer $Q_{\parallel}$ is primarily determined by the primary beam energy, and $Q_{\parallel}$ in turn defines the typical probing depth. Thus by varying the energy, one may change the properties of loss features in a spectrum of loss features. The solid lines in Figure 9 show the spectra for different primary energies for the surface after 500 L H exposure. The spectrum with 21 eV primary energy shows a somewhat reduced bare phonon peak whereas the spectrum with 4 eV primary energy has a much higher bare phonon peak compared with the 9 eV spectrum. Note that the middle spectrum is identical to spectrum d) in Figure 8. Qualitatively the physical explanation of these spectra is as follows. For higher primary energy, the probing depth is larger and the depletion layer is a smaller fraction of the probed volume. Thus the unscreened phonon peak intensity is relatively smaller. The opposite holds for lower primary energies.

Theoretical Modeling for Sample B

To gain a more quantitative knowledge of the space charge layer, a theoretical calculation is useful. Three approaches could be used to model the loss spectrum. In principle, one can solve the Schrödinger equation and Poisson's equation self-consistently to obtain the charge density profile, then construct a nonlocal theory

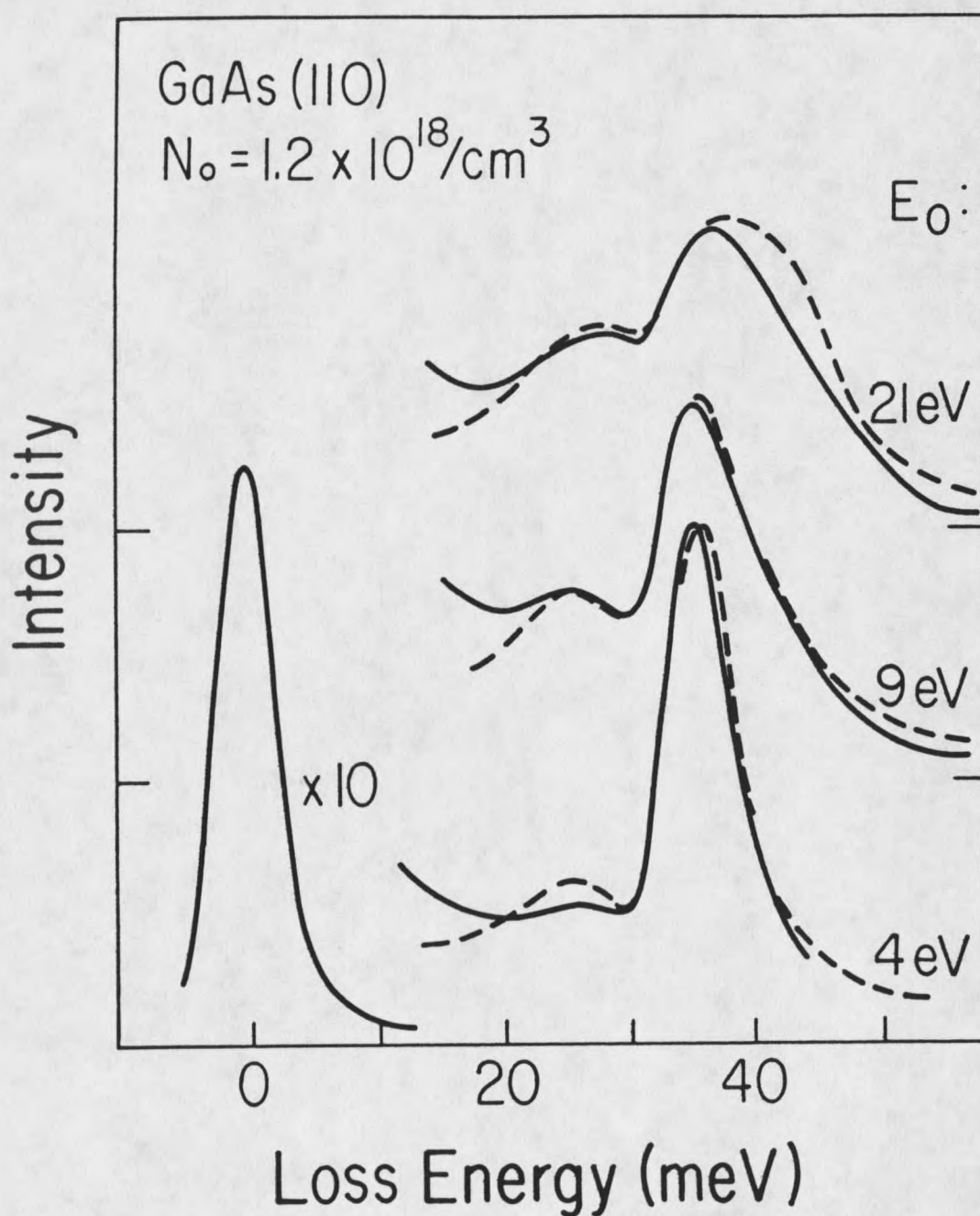


Fig.9

The HREELS spectra of GaAs(110) surface for different primary energy after the hydrogen exposure. The dashed lines are calculated spectra with bulk carrier density of $1.2 \times 10^{18} / \text{cm}^3$ and a depletion layer thickness of 260 Å.

to calculate the response of the system²³. This fully quantum mechanical nonlocal theory is difficult to implement. A second approach is to use a self-consistent charge density profile together with a Lindhard dielectric function²⁹ and local response theory to calculate the spectrum.¹⁷ The third approach is what has been done for the first sample, ie. the two-layer model, or multilayer model of the charge density profile.

Here the last approach is employed to calculate the loss spectrum. The results will be compared to the experimental results and the theoretical results of the second approach as reported in Ref. 17.

The dielectric description of the system is similar to what is used for sample A except that a damping term in the dielectric function is added and that the bulk electron density n_0 is used as an adjustable parameter:

$$\epsilon_b(\omega) = \epsilon(\infty) - \frac{[\epsilon(0) - \epsilon(\infty)]\omega_{To}^2}{\omega^2 - \omega_{To}^2 + i\omega\gamma} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} \quad (4.11)$$

where γ is 0.3 meV as inferred from IR data and Γ is about 10 meV from the mobility of the sample. With Eq. (3.7), the loss function is then integrated together with the kinematic factor, for the geometry of 45° incident angle, over the allowed wave vector due to the finite size of the entrance aperture of the analyzer, to obtain the loss spectrum. To compare with experimental results, the calculated spectrum is convoluted with a Gaussian function with FWHM corresponding to the experimental value. The results are plotted in Figures 8 and 9 as broken lines.

In the calculation the depletion layer thickness d is a parameter. In order to fit the spectrum of the fresh-cleaved surface where the intrinsic depletion layer is present, we still need a finite d value of about 110 Å. This d is the thickness of an

intrinsic electron depleted layer due to the quantum mechanical effect. The value is quite large compared to that of about 32 Å obtained by extrapolating the self-consistent calculation of Ehlers *et al.*²² Matz and Lüth¹⁴ have reported a 150 Å "dead layer" for the doping of $3 \times 10^{17}/\text{cm}^3$, which is also much larger than the theoretical results.²² We have argued earlier that initial band bending is not the reason. Ehlers and Mills¹² have pointed out that the results for large electron concentrations are influenced significantly by the degree of donor ionization in the bulk. In their calculation, the degree of ionization is determined by combining the Fermi distribution with a fixed impurity energy level. In contrast, if 100% ionization is assumed, the results of the same calculation are much closer to the experimental value as discussed in Ref.17.

For spectra b, c and d of Figure 8, the depletion layer thicknesses are 180 Å, 200 Å, and 260 Å, respectively. Using Eq. (4.10), a band bending value of 0.57 eV is obtained for spectrum d, that of the surface after hydrogen exposure. The value agrees reasonably well with our UPS measurement (0.42 eV) and that reported in the literature³⁰ (0.55 eV). The derived band bending value for this case B is closer to the photoemission result than that found for case A. The closer agreement may be a result of using a line shape fit rather than simply the plasmon peak position fit. The line shape fit calculation is particularly important for interpreting the spectra of sample B since the line shape is more sensitive to the space charge parameters. This is also demonstrated in Figure 9 where the relative intensity rather than the peak position is more sensitive to the change of primary beam energy.

Note that, unlike the analysis for sample A, the bulk doping level n_0 is used as an adjustable parameter since the IR measurement provides only an upper limit of $1.5 \times 10^{18}/\text{cm}^3$. In fact, to obtain a reasonable fit for all the spectra in Figure 8 and 9, n_0 can not vary much; $1.2 \times 10^{18}/\text{cm}^3$ appears to be the best value. It is very

encouraging to find that the number is very close to the measured doping level ($1.3 \times 10^{18}/\text{cm}^3$). The prediction of the doping level also demonstrates that the two layer model can provide quite accurate information.

In trying to understand the response in more depth, a less abrupt space-charge profile is employed to calculate the spectrum, as discussed below. For a given band bending, Poisson's equation is solved to obtain the electron density profile in the regime of the Thomas-Fermi approximation and with the assumption of 100% donor ionization. This charge density profile was then used to calculate the loss function. To use the formulation developed by Lambin *et al.*³¹, the space-charge region is divided into layers so that the electron density can be treated as constant in each layer. The dielectric function of each layer takes the form of Eq. (4.6) with $\omega_p^2 = 4\pi e^2 n_i / m^*$, where n_i is the local electron density in the i -th layer. The effective dielectric function $\tilde{\epsilon}$ (see Eq. (3.7)) is³¹

$$\tilde{\epsilon}(Q_{\parallel}, \omega) = a_1 - \frac{b_1^2}{a_1 + a_2 - \frac{b_2^2}{a_2 + a_3 - \dots}} \quad (4.12)$$

with $a_i = \epsilon_i(\omega) / \tanh(Q_{\parallel} d_i)$, $b_i = \epsilon_i(\omega) / \sinh(Q_{\parallel} d_i)$ and d_i is the thickness of the i -th layer. For a typical band bending value of 0.3 eV which, in the Thomas-Fermi approximation, is equivalent to a depletion layer 180 Å thick, the calculated spectra of the two layer and multilayer approaches are compared with experimental data in Figures 10 and 11. Note, that the experimental curves are identical to spectrum b) in Figure 8. The results show that the multilayer model seems to smear out the structure in the spectrum due to its broad plasmon loss features. Three aspects are discussed which could lead to this broadening. First, in the model the space

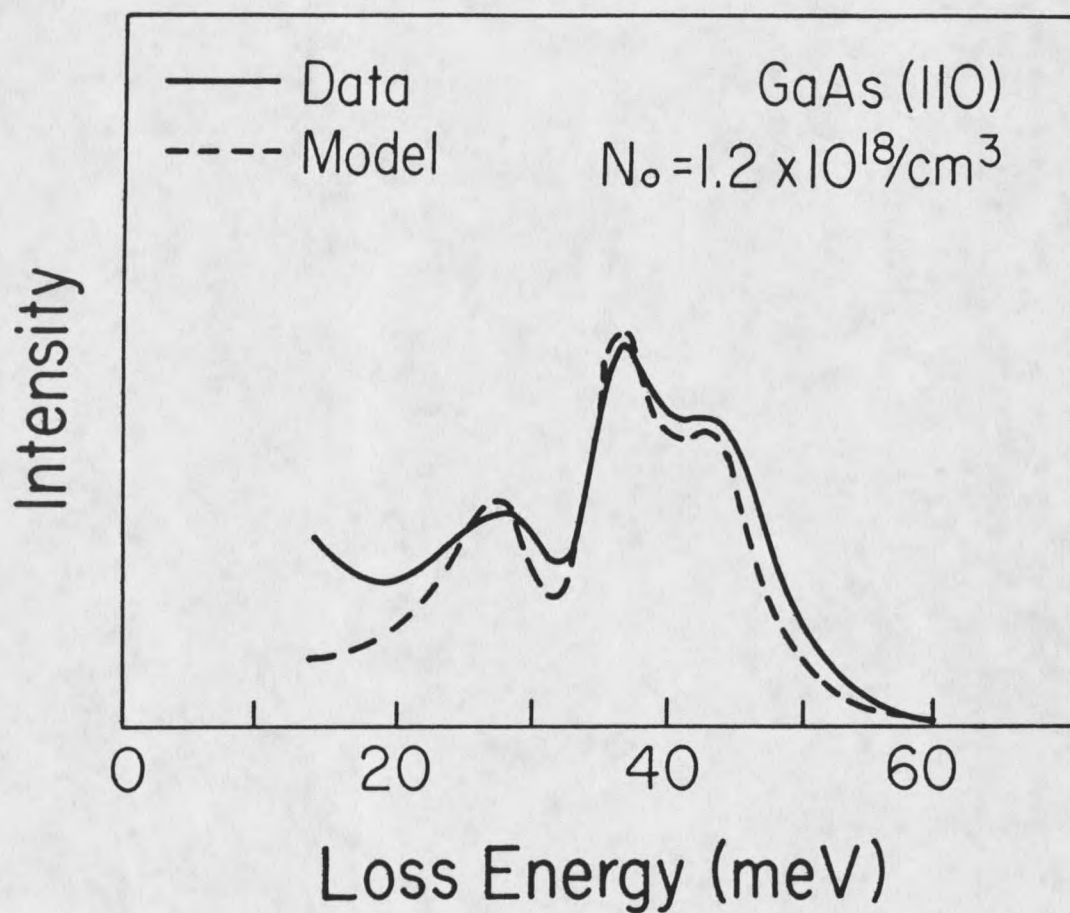


Fig.10 The calculated HREELS spectra for band bending of 0.3 eV using a two-layer model (dashed) is compared with experimental data (solid).

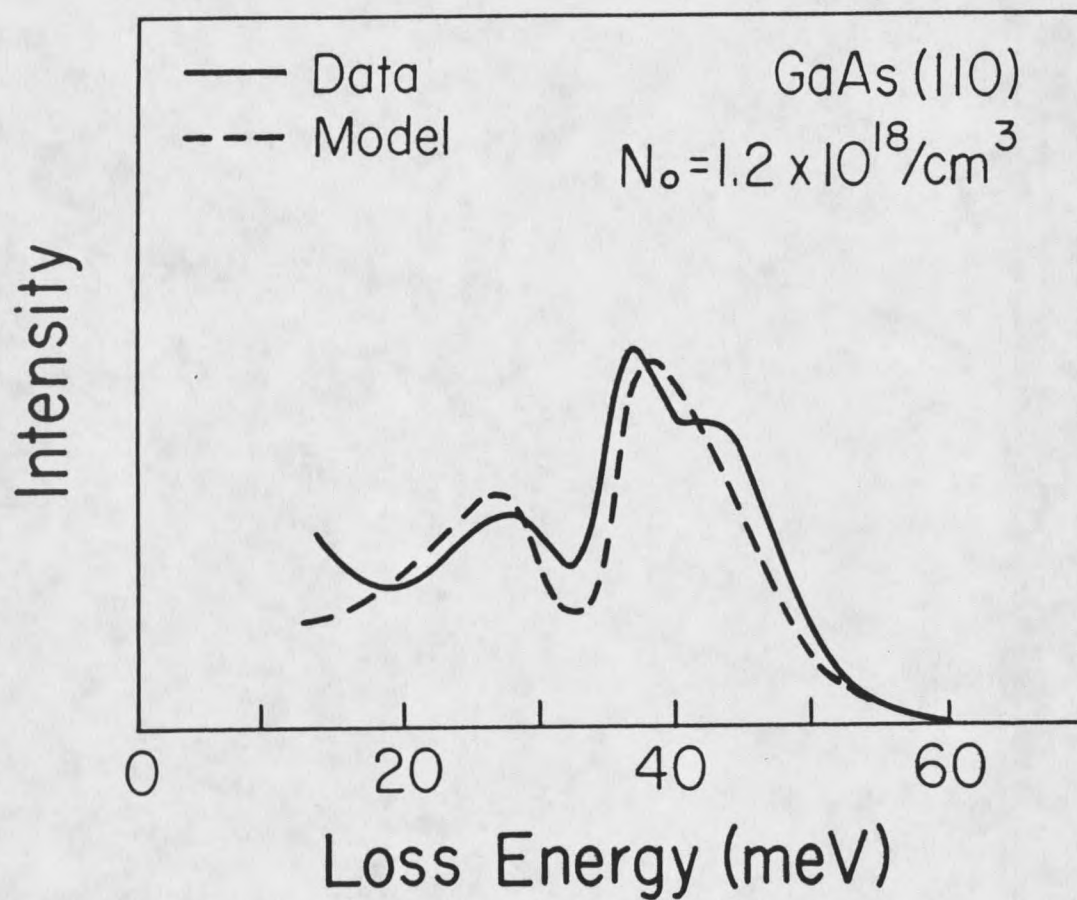


Fig.11 The calculated HREELS spectra for band bending of 0.3 eV using multilayer model (dashed) is compared with experimental data (solid).

charge region is divided into many layers in which the electrons oscillate with a local plasmon frequency. The total loss peak is the envelope of the local plasmon in each layer which broadens the loss in addition to the broadening due to Drude damping. The broadening is solely due to the local response theory. A nonlocal theory is needed to examine to what extent the local theory affects the broadening. Second, the electron density profile derived from Thomas-Fermi approximation may not be realistic. The possible failure of the Thomas-Fermi picture is not surprising since the electron's deBroglie wavelength is larger than the screening length in this highly doped semiconductor.²² Finally, the Drude response may not be adequate since it ignores the intrinsic dispersion of the plasmon.

To elucidate the effect of the Thomas-Fermi approach, the results of Hermanson's¹⁷ calculation are included for comparison in Figures 12, and 13. The model uses a self-consistent free-carrier profile together with the Lindhard description of the local dielectric response. The experimental data (open circle) in Figures 12 and 13 are identical to those of Figures 8 and 9. To fit these data with the latter model, the depletion layer thicknesses needed are generally smaller than for the two layer model; however, note that these values do not include the intrinsic electron free region. In terms of the measurable value of band bending, the value predicted is 0.52 eV, close to the result of the two layer model. In Figure 14, different model calculations are predicted by Hermanson. The experimental curve (solid) is the same as curve b in Figure 12, with a depletion layer depth of 110 Å and an incident electron kinetic energy of 9 eV. When the full Lindhard response is replaced by the Drude model, the dashed curve is predicted. The remaining two spectra are obtained using a two-layer model. The long-dashed (dotted) curve is predicted by the Lindhard (Drude) dielectric response. The Drude response of the continuous charge density (dashed) has a weak shoulder on the high-energy side of

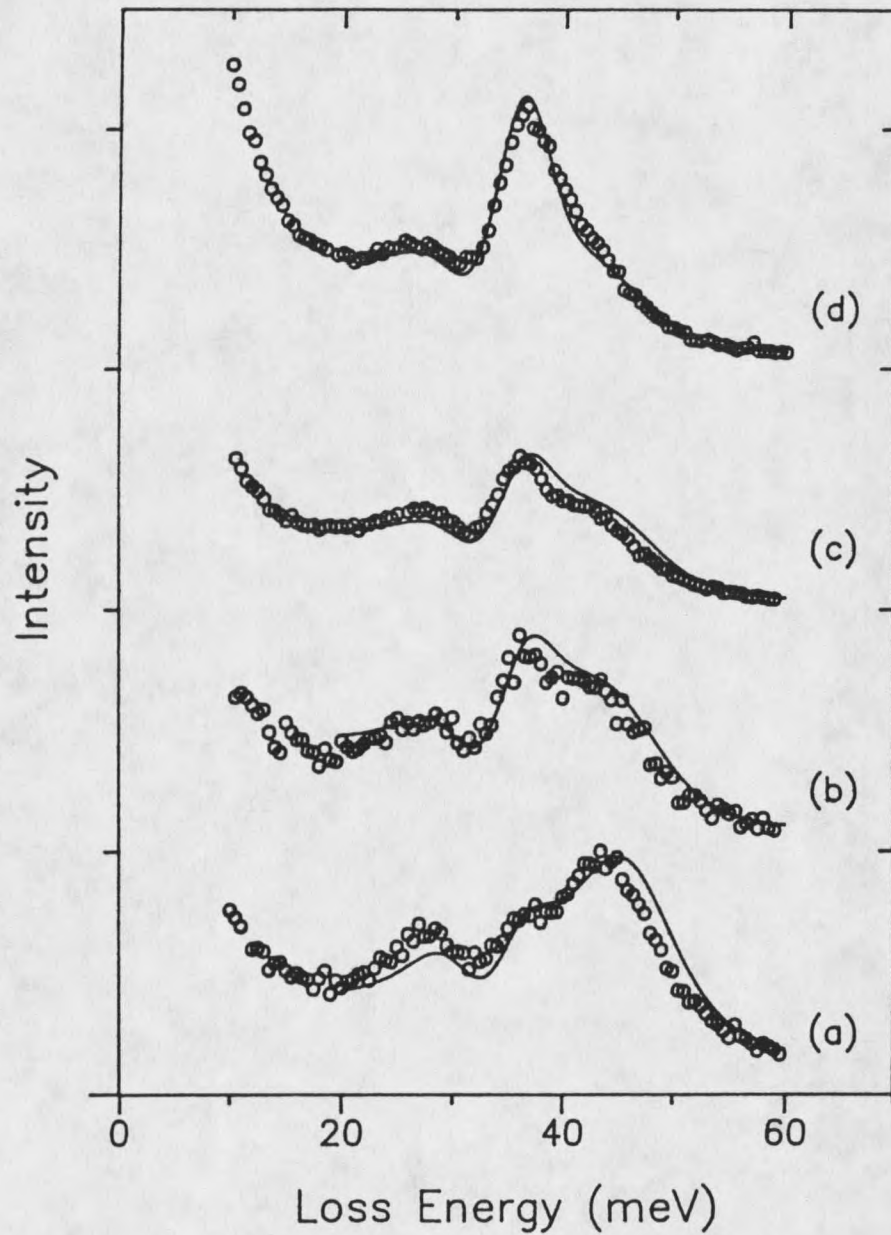


Fig.12

The HREELS spectra for the cleaved GaAs(110) surface. The experimental curves (open circles) are identical to those in Figure 8. The solid lines are the theoretical spectra calculated by Hermanson. $1.3 \times 10^{18}/\text{cm}^3$ is the bulk carrier concentration, and the depletion layer thickness assumed for each spectrum is 70 Å, 110 Å, 125 Å and 230 Å, respectively.

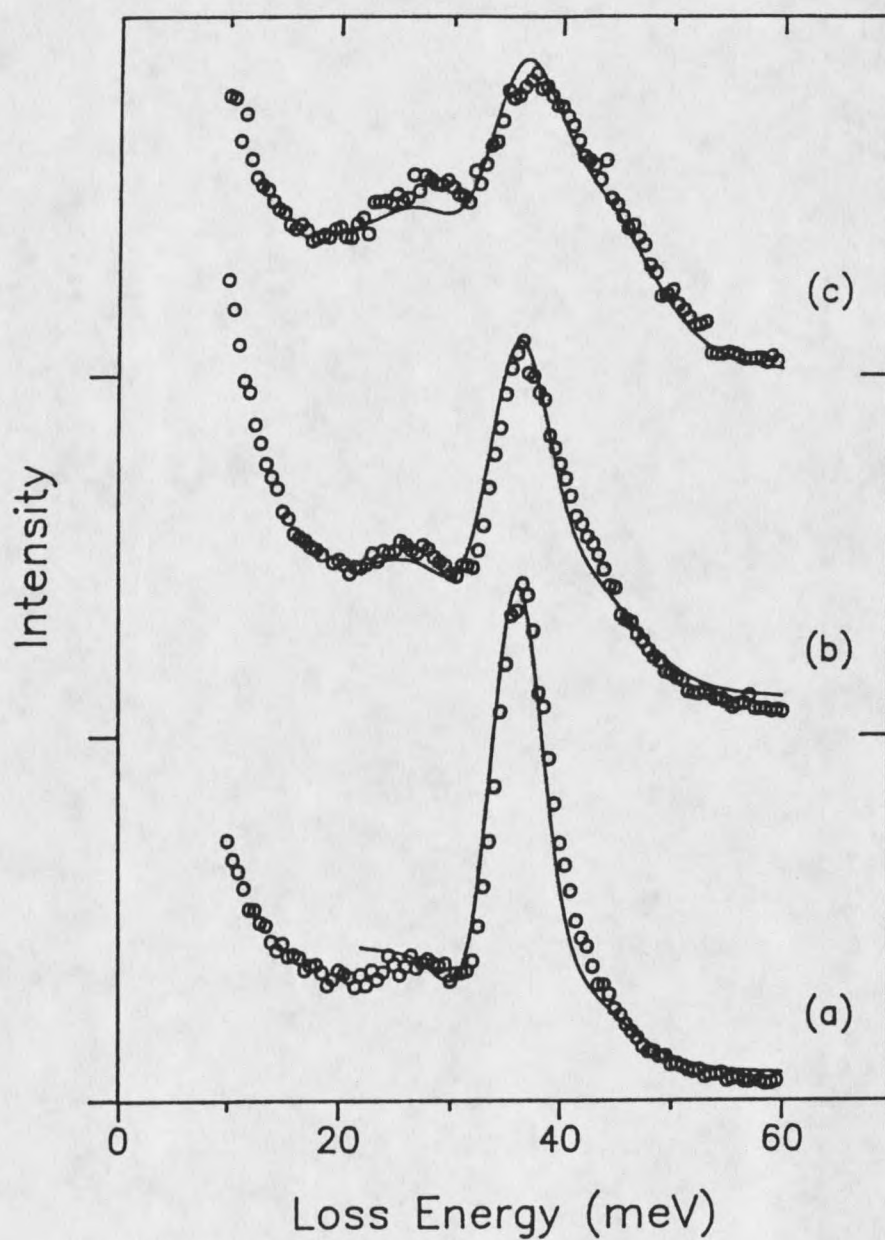


Fig.13

The HREELS spectra for different primary energies after hydrogen exposure (open circle). The solid lines are calculated spectra (after Hermanson) with a bulk carrier density of $1.3 \times 10^{18}/\text{cm}^3$ and a depletion layer thickness of 230 Å. Primary energies are (a) 4 eV, (b) 9 eV, (c) 21 eV.

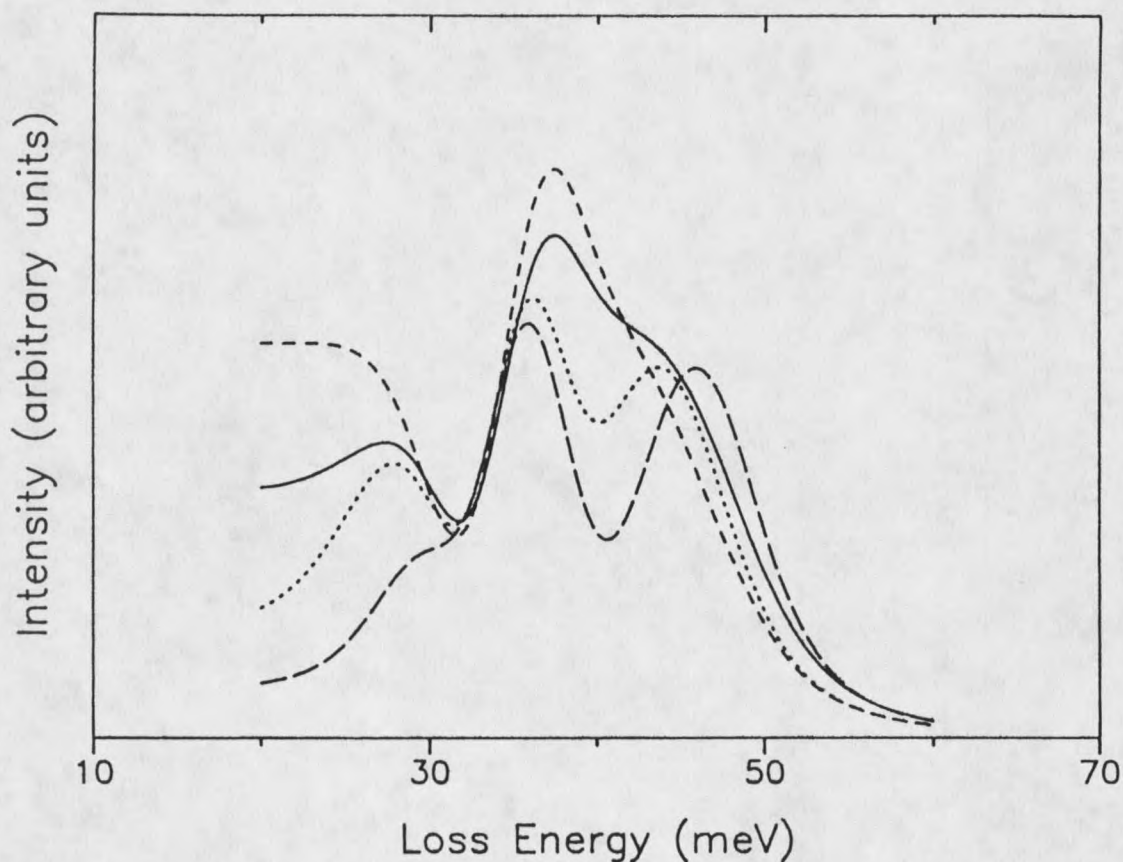


Fig.14 The calculated HREELS spectra (after Hermanson) for various models of the free-carrier profile and dielectric response. The solid curve is the same as (b) in Fig.12, with a depletion layer depth of 110 Å and an incident electron kinetic energy of 9 eV. When the full Lindhard response is replaced by the Drude model, the dashed curve is predicted. The remaining two spectra are obtained when the self-consistent free-carrier profile is replaced with a step function; the long-dashed (dotted) curve is predicted by the Lindhard (Drude) dielectric model.

the unscreened-phonon. This is because the Drude model does not contain k (wave vector) dependence in the dielectric function. In the step model, both the Lindhard and the Drude response give structures which are too narrow; but surprisingly, the Drude response predicts peak positions which are in better agreement with the full theory. One defect of the two layer model is that it contains no regions of intermediate charge density that would broaden the structure. For a given bulk carrier density, the negative dispersion of the Drude response compensates for the narrow structure due to a stepped charge density profile, so it gives better overall results. This also explains the good agreement of the earlier step model calculation with the experimental spectra.

The spectra presented in this study also contain an interesting feature which has not been previously reported: the 16 meV gain peak noted in Figure 7. This peak is not an artifact of spectrometer tuning since it is observed on two spectrometers and by workers in another laboratory.³² It is also unlikely that the peak is anomalous in the sense that only its gain is observed. In fact, the elastic peak is asymmetric and the background on the loss side is higher; therefore, the loss peak of the resonance is probably buried in the background. In addition, this gain peak disappeared when the sample was cooled down to 80 K, providing evidence that this is a normal dipole excitation. The intensity of this peak is so strong that it can only be a collective excitation. The fact that its intensity does not change like that of a plasmon with respect to primary energy could mean that the excitation has a different spatial structure. Moreover, since surface contamination does not change this peak, the excitation is probably not the type of surface phonon found on Si(111)³³. As a result of the above consideration, we suggest that this peak is due to a surface optical phonon mode. Recently, Harten *et al.* reported an observation of two flat optical modes at 10 meV and 13 meV in their helium

atom scattering experiments on GaAs(110).³⁴ These two modes are not yet understood although they could be interpreted in terms of localized atomic vibrations. The mode observed in our experiment is at a slightly higher energy. Since possible dispersion was not looked for in the measurements it cannot be concluded that this is the same mode observed in atom scattering. Both results suggest that surface phonon structures exist in addition to the Fuchs-Kliwer phonon. More measurement and theoretical calculations need to be done to address this issue.

CHAPTER 5

COUPLED PLASMON AND PHONON MODES IN ACCUMULATION LAYERS

Introduction

It has been shown in Chapter 4 that HREELS is a unique probe for studying the coupled plasmon and phonon in a depletion type space-charge layer. Most semiconductor surfaces fall into this category and many investigations have been carried out as referenced in Chapter 4. However, few studies are found that are focused on the other type of space-charge layer, the accumulation layer. The main reason is that most semiconductor surfaces can only form a depletion layer in the absence of an external field. One example of an accumulation layer that has been studied is the ZnO(0001) oxygen face.³⁵⁻³⁸ A very strong accumulation layer is formed by exposing the surface to atomic hydrogen. The band bending induced by hydrogen is about 1.5 eV, which ensures a very strong and narrow accumulation layer. The electron movement perpendicular to the surface in the layer is quantized to form sub-bands; thus the plasmon behaves like a two-dimension excitation.

The InAs(110) cleaved surface offers another example of an accumulation layer at a free surface. In contrast to the case of ZnO, the band bending is small, about 0.13 eV for oxygen adsorption³⁹ and 0.2 eV for hydrogen adsorption, as revealed by our UPS measurement. Such a small potential together with the small effective mass

provides an accumulation layer about 100 Å thick, so the sub-bands here are not as important as in the ZnO case. In addition, for a typical momentum transfer $Q_{\parallel}$ in our experiments, $Q_{\parallel}d$ is not very small, where d is the width of the accumulation layer. Thus the plasmon behaves more like a three-dimension excitation. Since the probing depth is comparable to the accumulation layer thickness, the details of the electron density profile will affect the HREELS spectrum. From this standpoint, our results provide a very good reference for testing theoretical models.

Experimental Results

The experiment was performed with a Leybold-Heraeus model ELS-22 spectrometer. The base pressure was 1×10^{-10} torr during the measurements. The InAs crystal was n-type with a free carrier density of about $1.3 \times 10^{16}/\text{cm}^3$ as measured by the Hall effect. The hydrogen exposure was made with the sample not in the line of sight of the hot tungsten filament. The surface Fermi level pinning was obtained by monitoring the In4d core line shift in the He lamp UV photoemission spectrum.

Figure 15 shows the HREELS spectra of the InAs(110) surface at different stages of accumulation layer formation achieved by successive hydrogen exposure. The impact energy of the electron beam is 22 eV and the angle of incidence is 45° . The scattered electrons are collected in the specular direction. Spectral changes as time elapsed were not observed (in the scale of two hours). This is because a) a much lower background chamber pressure was achieved, and b) most importantly the interaction of H with the surface is much weaker at room temperature on InAs(110) than on GaAs(110). As shown in Chapter 6, H does not adsorb on the InAs(110) surface at room temperature as readily as it does on GaAs(110) surface.

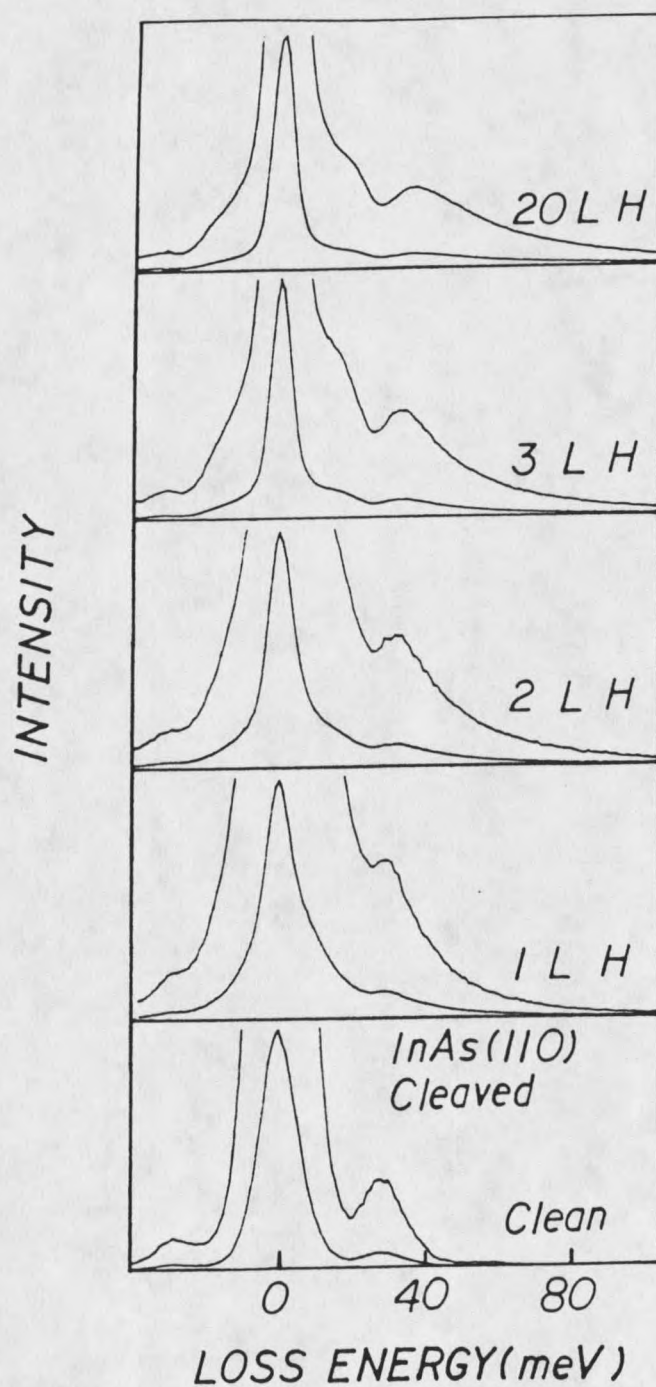


Fig.15

HREELS spectra of n-type InAs(110) clean cleaved and hydrogen-exposed surfaces. The primary beam energy is 22 eV and the angle of incidence is 45°.

As shown in Figure 15 for the clean cleaved surface, the optical phonon at 29 meV and corresponding gain are clearly resolved. The FWHM of the quasi-elastic peak is about 13 meV. This value is significantly larger than that of the top spectrum in Figure 15 taken on the surface after 20 L of hydrogen exposure. This indicates that the instrumental FWHM is much smaller than 13 meV. The broadening of the quasi-elastic peak of the clean surface is due to the excitation of conduction-band free-electron plasmons. Such phenomena have been studied by many authors.^{27,40,41} With the electron density of $1.3 \times 10^{16} / \text{cm}^3$, the surface plasmon energy is calculated from Eq. (4.2) to be 7 meV. Considering the fact that the electrons are depleted from the surface region even when the bands are flat as discussed earlier for GaAs, the plasmon energy will shift to smaller energy. Thus the plasmon loss is buried in the quasi-elastic peak. A realistic calculation of the FWHM needs to take multiple excitation into account⁴⁰ as well as instrumental resolution.

When as little as 1 L of hydrogen exposure is made, surface plasmon excitations produce a very large wing on each side of the elastic peak and the phonon is damped; with 2 L hydrogen, the plasmon can be resolved as a bump and the phonon moves towards higher energy. As the hydrogen exposure increases, both peaks move towards higher energy and reach a final position at about 20 L. At the saturation stage, the plasmon and phonon are strongly coupled and it is impossible to identify the losses as simple plasmon or phonon type. The final band bending after hydrogen exposure is about 0.23 ± 0.05 eV downward as measured with UPS.

The spectra in Figure 15 can be interpreted in terms of accumulation layer formation. The development of the plasmon loss is directly related to the electron density increase in the accumulation layer as hydrogen is adsorbed.

An interesting feature, for surfaces with a fairly strong accumulation layer, is

that the widths of the two coupled losses are much larger than the quasi-elastic peak. For a mobility of about $18500 \text{ cm}^2/\text{V s}$, the Drude damping constant is approximately 2-3 meV. This is obviously too small to account for the width. Two possible contributions are discussed here. First, the charge density in the accumulation layer is highly non-uniform while the thickness of this layer is comparable to the probing depth of the incoming electron. Thus, the details of the charge density profile will affect the spectrum. From the standpoint of local response theory, if one divides the space-charge region into sub-layers, the local plasmon in each sub-layer will be at different energy due to electron density differences. The overall plasmon loss is the envelope of these sub-layer plasmons including the interference among them. The second contribution to the plasmon width is due to the instrumental resolution. In the HREELS measurements, with a finite analyzer collecting slit, the $Q_{\parallel}$ transfer is not unique; instead, it spreads over a finite range. If the plasmon has a very strong dispersion, the resulting plasmon loss will also be broad.

Figure 16 shows spectra obtained after the surface is exposed to 100 L of hydrogen. The primary energy E_i is varied between 1 and 47 eV. This set of curves utilizes the tunability of the probe depth in HREELS to study the spatial localization of the plasmon and phonon modes. For lower primary energy (less than 5 eV), the unscreened phonon at 29 meV becomes very strong, and the coupled plasmon-phonon mode can only be resolved as a wide bump with an energy position around 55 meV. For those spectra with primary energies higher than 5 eV the structures are similar. The 5 eV primary beam spectrum is in a transition region; the bare phonon is not resolved and the plasmon energy is not as high as found in the spectra obtained at lower primary energy.

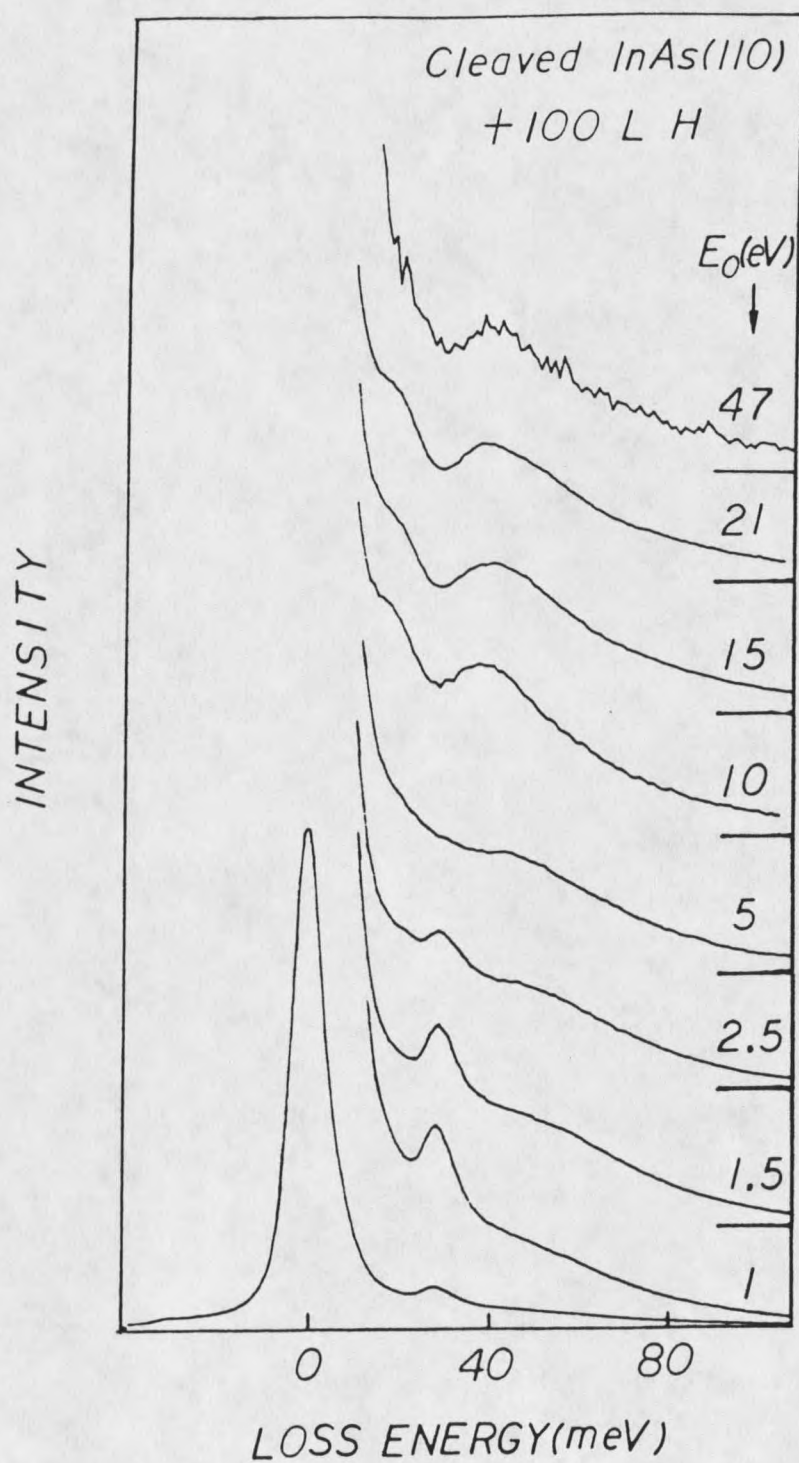


Fig.16

HREELS spectra of InAs(110) cleaved surface after 100 L H exposure with different primary energies. The angle of incidence is 45° .

Theoretical Discussion

To aid the understanding of the spectra in Figures 15 and 16, a model calculation is helpful. The widely adopted two layer model is not adequate in this case since the electron density changes too rapidly near the surface. Thus we include the calculated results by Hermanson⁴² in Figures 17, 18 and 19. The model calculations are based on a self-consistent free-carrier profile together with the Debye-Hueckel description of the local dielectric response. The details of the model and calculation are given in Ref. 42. The free-carrier density profile is shown in Figure 17 with a surface charge deficit of 1.2×10^{12} electrons/cm² which is equivalent to 0.26 eV band bending, close to our U*PS measurement. In Figure 17 the density unit is 1.83×10^{18} /cm³ and the length unit is 81.8 Å. One sees that a fairly high electron density extends from about 40 Å to 160 Å below the surface; the highest density is about 8×10^{17} cm⁻³ at a depth of 78 Å.

Figure 18 displays the calculation (after Hermanson⁴²) of the loss spectrum, including features due to the coupled plasmon and phonon as the accumulation layer forms. By a comparison to the spectra in Figure 15, the overall features are predicted correctly as the surface charge (or equivalently the band bending) varies. Note that the increase of surface charge required to fit the experimental data is in proportion to the increase of hydrogen exposure for the lower four spectra. This linear relation is expected for lower exposures as discussed earlier in Chapter 4, which justifies the applicability of the model in this respect.

Figure 19 shows calculated spectra for a surface charge deficit of 1.2×10^{12} /cm² with primary energy as a parameter. The basic structures noted in the experimental data in Figure 16 are reproduced in Figure 19. The physical insight revealed is as

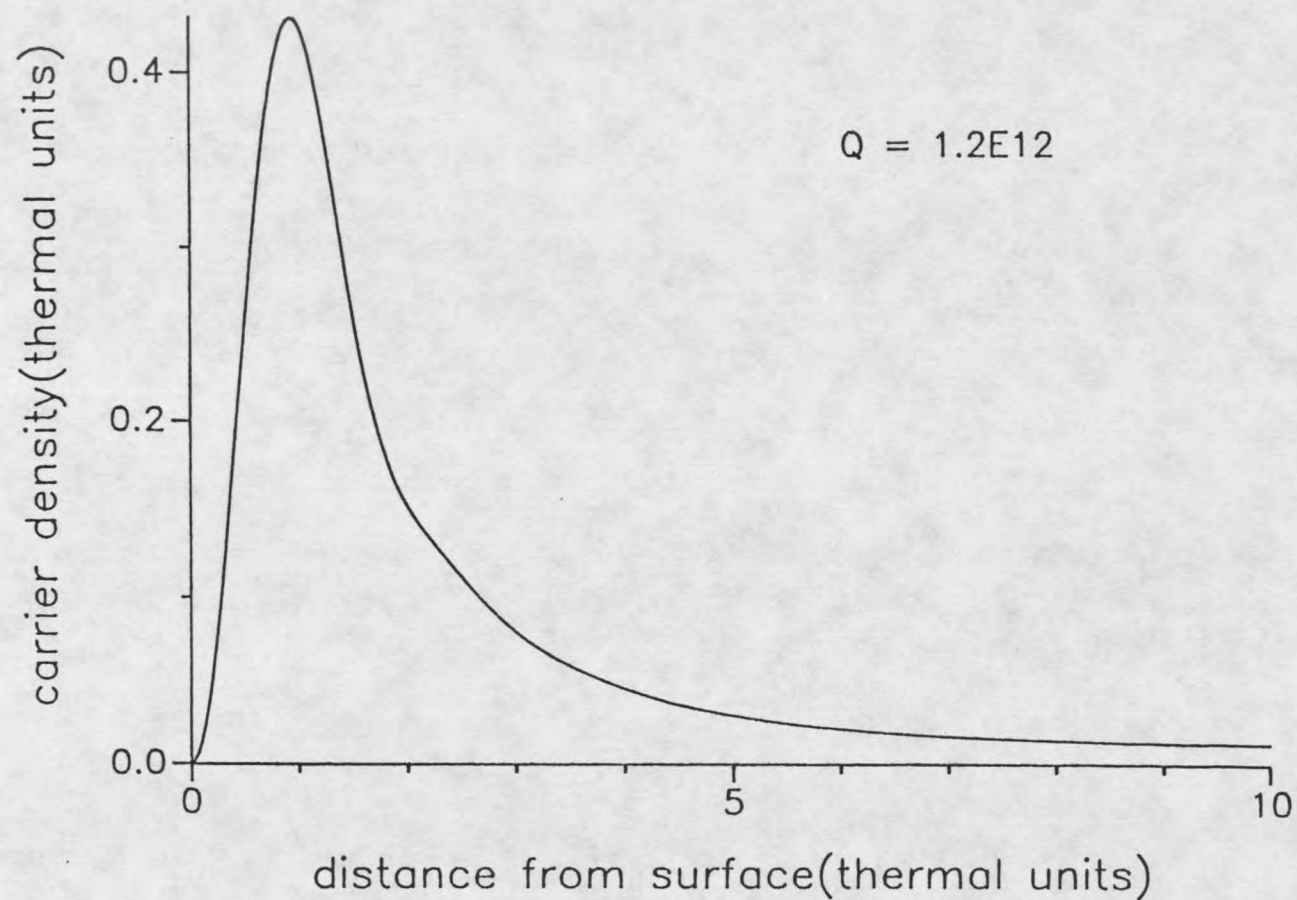


Fig. 17

The charge density profile $n(z)$ of the self-consistent calculation (after Hermanson). The surface charge deficit used is 1.2×10^{12} electrons/cm³ which corresponds to 0.26 eV band bending.

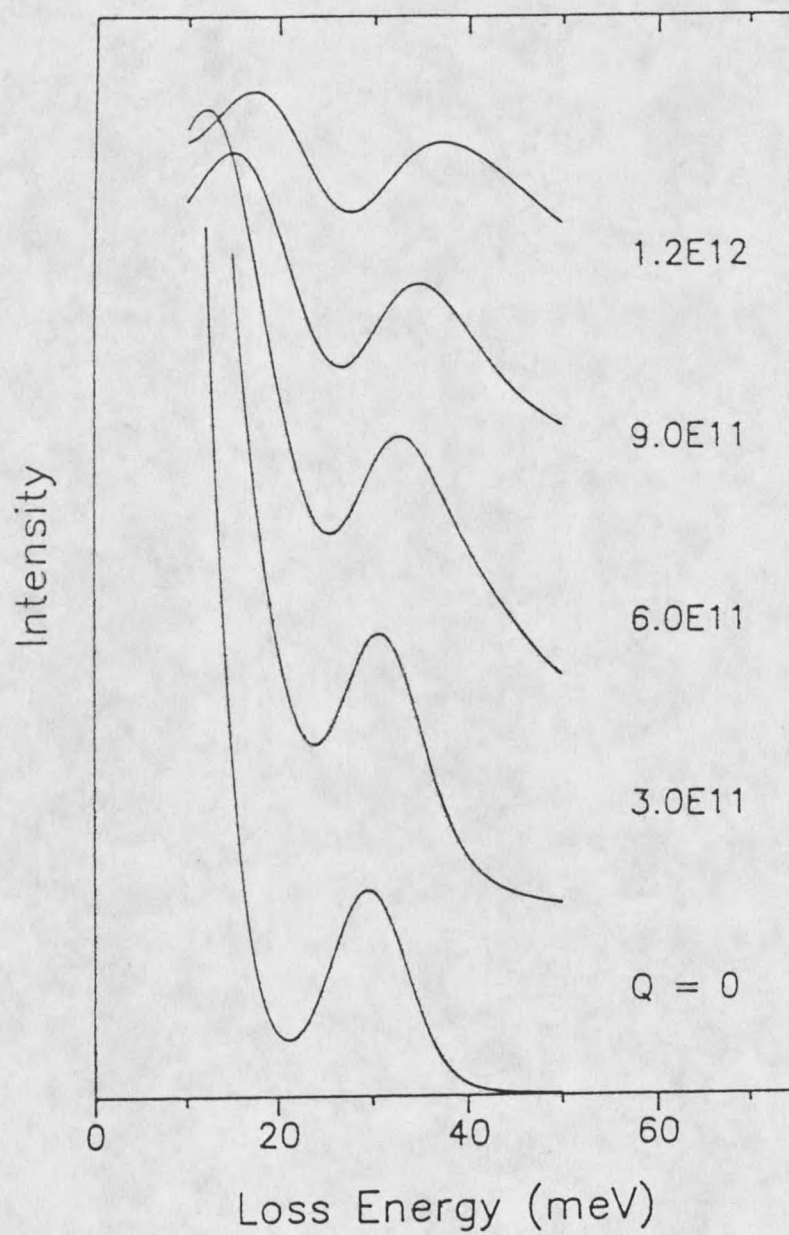


Fig.18

Calculated spectra with different surface charge deficit for 21 primary energy (after Hermanson).

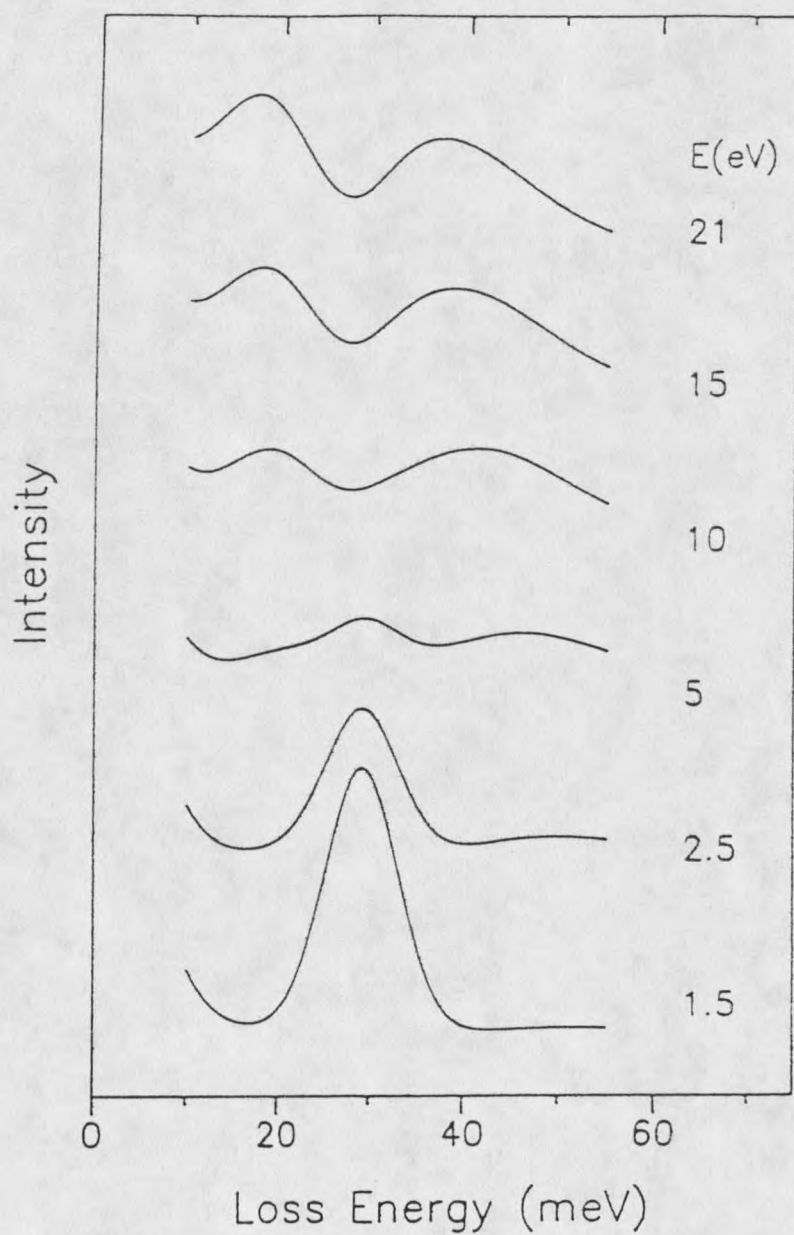


Fig.19

Calculated spectra with different primary energy and fixed surface charge deficit of 1.2×10^{12} electrons/cm³ (after Hermanson).

follows. For low energies, the probing depth is relatively small (140 Å for primary energy of 2 eV), so a fairly wide portion of the probing depth, about 40 Å (see Figure 17), extends over the intrinsic electron depleted region near the surface. Thus the unscreened phonon is observable. Also, the high electron density portion contributes more when the probing depth is small; this results in the movement of the plasmon loss to higher energy. When the primary energy is higher, the probing depth becomes large (440 Å for 20 eV primary energy). As a consequence, the relative weight of the unscreened phonon is smaller, and so is the contribution of the high density electrons near the surface. An interesting point is that the high electron density in the accumulation layer itself screens the bulk of the sample so that the unscreened phonon below the space-charge layer cannot be seen. In fact, for a primary energy above 5 eV, two coupled plasmon-phonon modes are seen in Figures 16 and 19, and their dispersion is weak because the field of the incoming electron samples a region that is large compared with the thickness of the accumulation layer.

To justify that the structures discussed so far are not due to hydrogen or adsorbed contaminants vibrational modes, an extended-energy-range HREELS spectrum is shown in Figure 20. The energy range of hydrogen-substrate vibration and other common contaminant vibrations, such as C-O, C-H and O-H, are above 100 meV. The spectrum shows no evidence of these contaminants. The contamination in the worst case is less than 10% of a monolayer which is not enough to produce the strong loss lines in the lower energy range as shown in Figure 15 and 16.

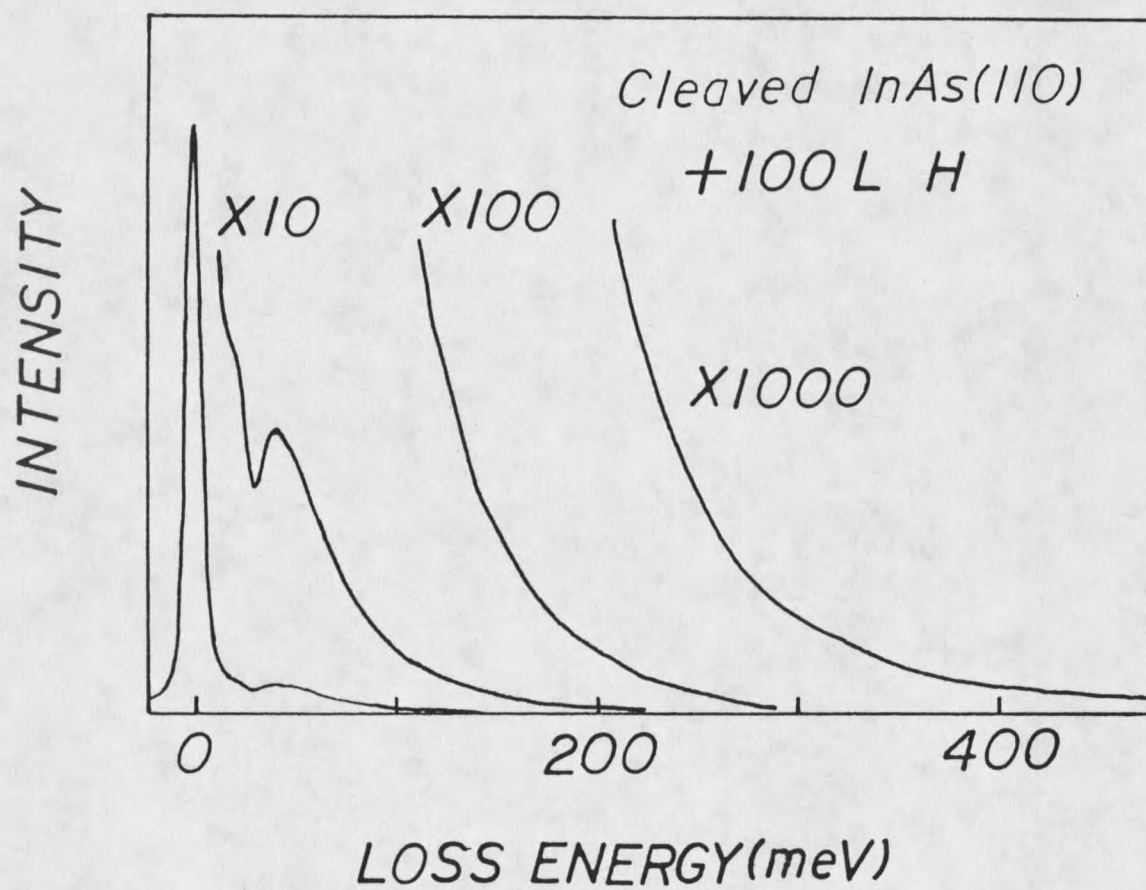


Fig.20

The extended energy range HREELS spectrum after 100 L H exposure.

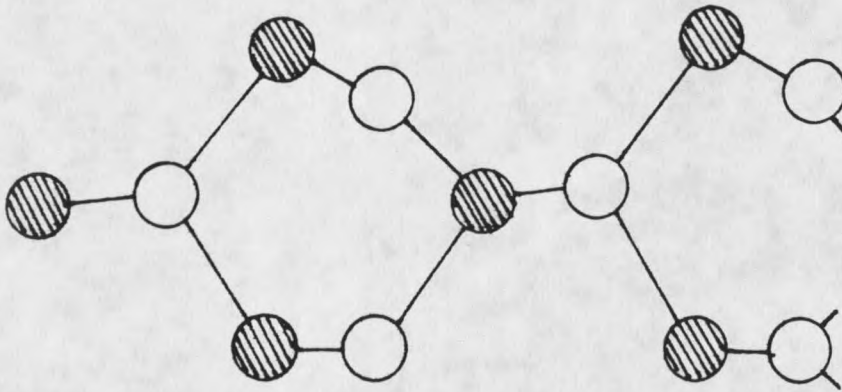
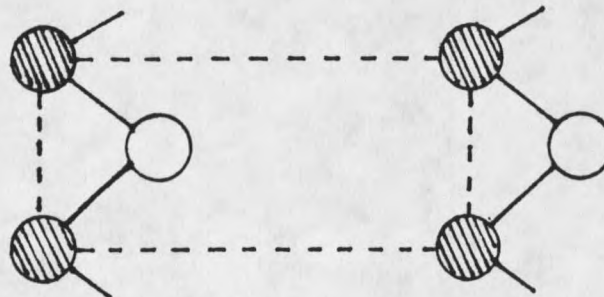
CHAPTER 6

HYDROGEN ADSORPTION ON CLEAVED AND SPUTTERED SURFACES OF III-V SEMICONDUCTOR

Introduction

In Chapter 4 and 5, hydrogen was used to modify the surface Fermi-level pinning. The conduction band electronic behavior and interaction with the phonons was presented. However, the nature of the electronic structures and chemical properties of the surface were not discussed. In this chapter, the focus will be on the study of H-substrate stretch vibrations which can elucidate some of the electronic and chemical properties of the surface. Most surface spectroscopic techniques are not sensitive to H; for example, its effects on LEED are very small due to the small size of its charge. HREELS however is an excellent probe for H adsorption studies.

After two decades of study, the atomic structures of the clean cleaved surfaces of III-V semiconductors are reasonably well understood: the truncated surface undergoes a relaxation, regardless of the preparation procedure (cleave or sputter-anneal), with approximately 29° rigid rotation of plane formed by the surface anions and cations as shown in Figure 21.⁴³⁻⁴⁷ This surface atomic geometry change is driven by the rehybridization of the surface cation and anion

a)Side view**b)Top view****Anion****Cation****Fig.21** The atomic structure of III-V semiconductor (110) face

orbital from their sp^3 configuration to sp^2 and p^3 , respectively.^{47,48} Accordingly the cation dangling bond is nearly empty and the anion dangling bond is almost filled. This process lowers the total energy of the system by about 1.2 eV per pair of surface atoms.⁴⁵ The relaxation reduces the electronic energy of the occupied surface states (the anion dangling bonds) at a cost in elastic energy associated with the corresponding atomic motions. This relaxation picture has been verified for all (110) faces of III-V compounds with little apparent correlation with the ionicity of the crystals.⁴⁴

The adsorption of foreign atoms affects the substrate electronic structure since chemical bonds are formed between adsorbate and substrate. If the energy gain of the chemisorbed system is greater than that of the reconstructed surface, the surface relaxation is modified or healed. The Sb-GaAs(110) system provides an example of this healing process. The Sb atom takes the position that the next-layer Ga and As would have taken, with the substrate close to its unrelaxed position.⁴⁹ Hydrogen adsorption on cleaved GaAs(110) and InP(110) surfaces has been reported to change the substrate relaxation.⁵⁰⁻⁵² One of our motives in the current study is to investigate the substrate relaxation change by hydrogen chemisorption on six III-V semiconductor cleavage surfaces.

The chemical properties of the semiconductor surface is another important issue. The interactions of gases with semiconductor surfaces have great impact on device characteristics and performance. Examples of such interaction are the passivation of surface states, plasmon etching in device fabrication, and oxide formation on surfaces. For some adsorbates this interaction may be complex. For example, the oxidation of the clean GaAs(110) surface has been studied for many years, but there has not been direct and conclusive evidence in support of a particular oxidation mechanism. Models proposed for oxygen binding to As,⁵³ Ga,⁵⁴

or adsorbed in a bridge-bond position⁵⁵ have been reported. Aside from the practical interests of hydrogen interactions with semiconductor surfaces, H chemisorption is relatively easy to understand and to model in theoretical calculations because of its simple electronic structure. Thus a thorough understanding of this interaction will provide background for a more complex chemisorption system.

The study of hydrogen adsorption has drawn much attention in the last ten years. Some results will be briefly reviewed. Molecular hydrogen does not interact with cleaved GaAs(110) surfaces.⁵⁶ HREELS studies have shown that atomic hydrogen adsorbs on both surface Ga and As atoms on cleaved⁵⁷ and sputter-annealed GaAs(110) surfaces.⁵⁸ The interaction can be characterized in two stages:⁵⁰ first, an adsorption which saturates with one hydrogen per surface atom, then a dissociation of arsenic with mainly arsenic hydride desorbing off the surface. It has been suggested that chemisorbed hydrogen heals the substrate relaxation for GaAs(110)⁵⁰⁻⁵² and InP(110).⁵¹ Studies of H adsorption on other III-V compounds are not as extensive as those for GaAs. Schaefer reported the case of H adsorbed on cleaved InP(110).^{59,60} It was observed that on the cleaved surface hydrogen adsorption yields a dominant In-H stretch in the initial stages, whereas the P-H stretch is the dominant feature for the lightly sputtered surface. Dubois *et al.* also reported a study of hydrogen on sputter-annealed InP(110) surfaces.⁵⁸ Although the results vary with different sample treatments, both In-H and P-H modes were observed for a well ordered surface. There are also reports of hydrogen adsorption on the sputter-annealed InSb(110)⁶¹ surface where both In-H and Sb-H stretch modes were weakly observed, and on cleaved InSb(110) where only the In-H bond was believed to be formed.⁶² It is generally believed that the H adsorbs on the surface atom via the dangling bonds of surface atoms.

These early studies reveal that the H adsorption behavior of the III-V cleavage surfaces is quite variable, while the clean surface reconstructions are similar. Another interesting point is that the adsorption properties are significantly affected by the sample preparation technique, e.g. cleaving versus sputter-anneal cycles. We have tried to investigate the hydrogen chemisorption on a lightly sputtered surface, and to understand the effects of surface condition on H adsorption.

Experimental Results

The experiments were performed with two Leybold-Heraeus model ELS-22 spectrometers. The atomic hydrogen exposures were produced by dissociation of hydrogen at a hot tungsten filament (1900°C) placed about 5 cm in front of the sample surface, which was in the line of sight of the filament. Because of the well known difficulty of knowing the true atomic hydrogen exposure, the dose was characterized by the molecular gas dose. The hydrogen exposure thus cannot be compared directly for different surfaces for quantitative purposes because two chambers were used and even in one chamber the conditions may not be exactly the same, especially the filament temperature. The details of the experimental procedure are described in Chapter 2.

The HREELS, XPS, LEED results are now presented for the following sequence of crystals: GaAs, GaP, InP, GaSb, InSb, InAs.

Gallium Arsenide

Figure 22 shows the HREELS spectra for clean cleaved GaAs(110) ((a) of lower panel), the surface exposed to 100 L hydrogen ((b) of lower panel), the sputtered

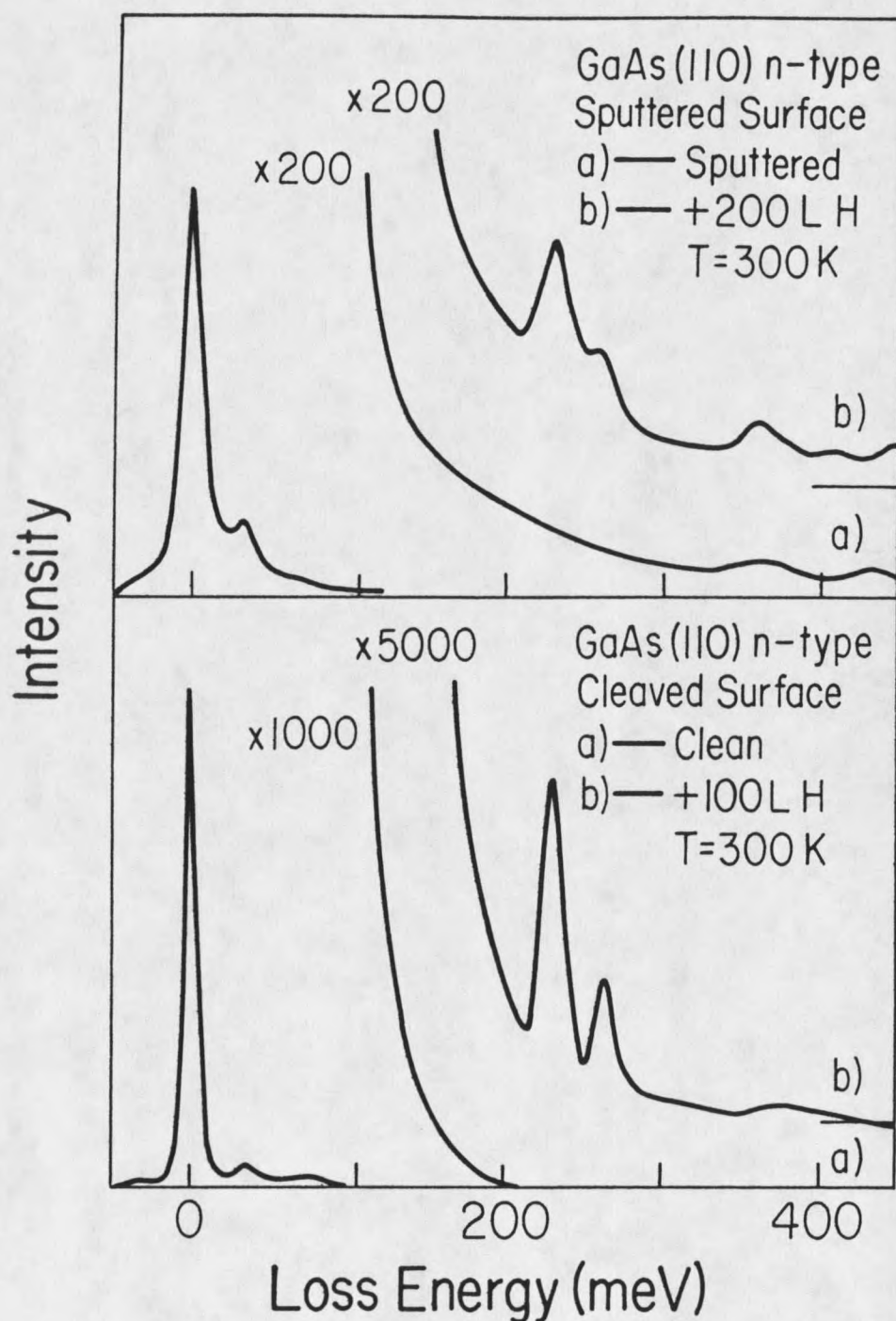


Fig.22

The HREELS spectra for GaAs(110) surface. Lower panel curve a) is as cleaved and curve b) is after 100 L H exposure. Upper panel curve a) is sputtered surface and curve b) is after 200 L H. The primary energy of the probing electron beam is 4.5 eV, with 60° angle of incidence.

surface ((a) of upper panel), and the subsequent 200 L hydrogen exposed surface ((b) of upper panel). The loss at 36 meV and its multiples are due to Fuchs-Kliwer phonons.^{57,58} This mode is insensitive to the crystal orientation⁵⁸ or to chemisorption of adatoms if the doping level is sufficiently low.

In terms of the hydrogen stretch modes, the results are similar to that of Lüth and Matz⁵⁷ except that the relative As-H stretch intensity is lower in our data. For the following reason the discrepancy is attributed to the use of samples with different doping levels. As discussed in Chapter 4 and 5, the phonon intensity is strongly screened by the free electrons in conduction band if the doping level is high. Apparently, the sample used in this investigation is heavily doped, so that the phonon intensity is only about 4% of the elastic peak. In Lüth's experiment, the sample was undoped so the phonon intensity was about 40% of the elastic peak. The difference between the As-H and Ga-H stretch energy is about 30 meV, which is close to the phonon frequency. Thus, one expects the 260 meV loss to contain the combination loss of the Ga-H stretch and the Fuchs-Kliwer phonon. In their data, 40% of the Ga-H stretch intensity should be subtracted from the 260 meV peak.

Hydrogen uptake was carefully monitored on the cleaved and the sputtered surface. The normalized intensities of Ga-H (open) and As-H (filled) stretch peaks are plotted as functions of H exposure in Figures 23 and 24 for cleaved and sputtered surfaces, respectively. From the uptake curve, one can monitor the coverage of the H atom on the surface. We see that the intensities of Ga-H and As-H stretches increase monotonically as a function of H exposure, which suggests that the adsorption kinetics and the sticking coefficient are unchanged during the entire exposure range. Furthermore, the relative ratio of As-H and Ga-H stretch intensities is essentially the same for all the exposures indicating there is no preferential adsorption. Comparing the intensity of the Ga-H stretch at 10 L H

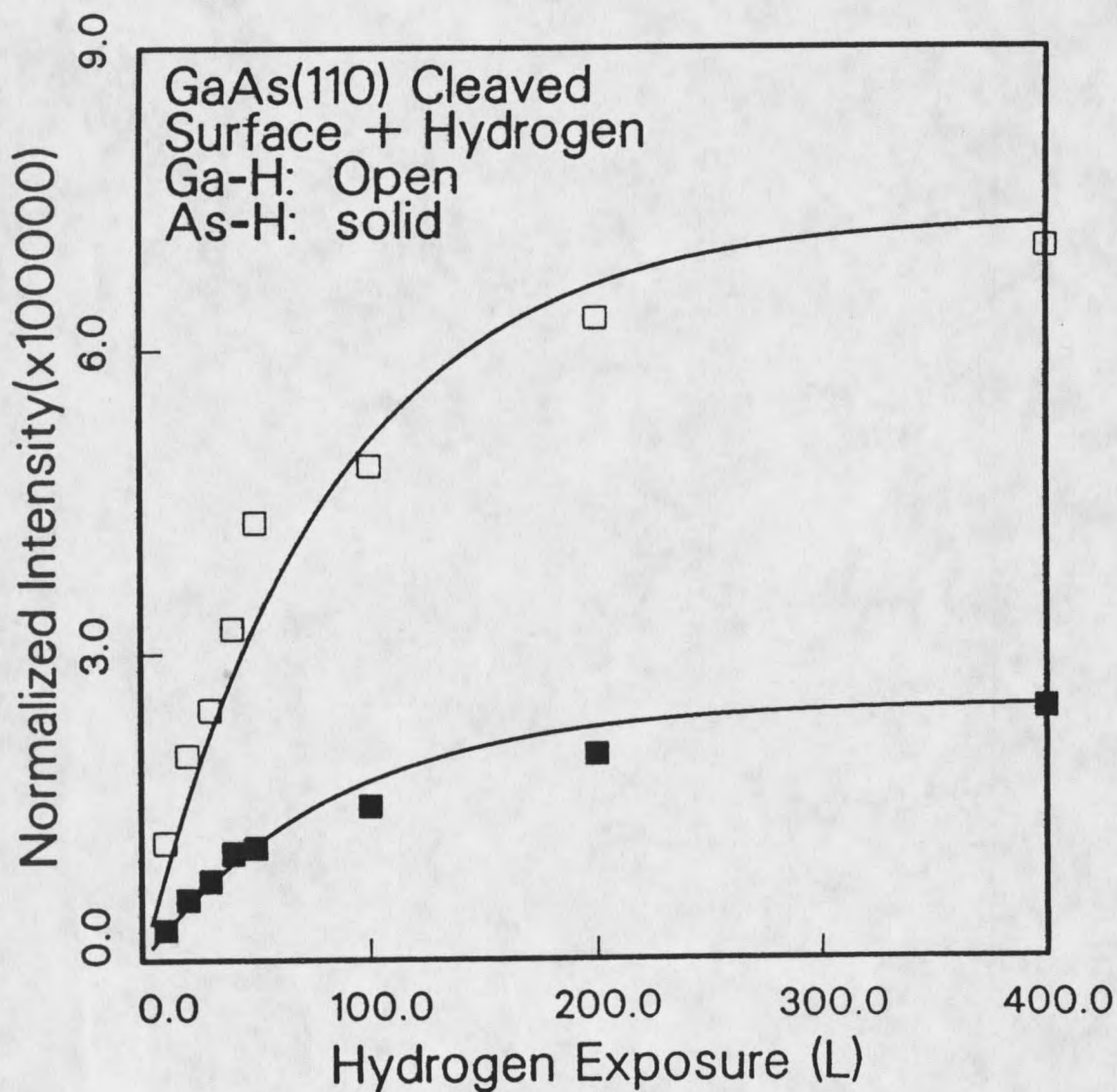


Fig.23

The H uptake behavior for the cleaved GaAs(110) surface. The Ga-H (open squares) and the As-H (solid squares) stretch intensities are plotted as a function of H exposure (L). The full lines are predicted from a model fitting.

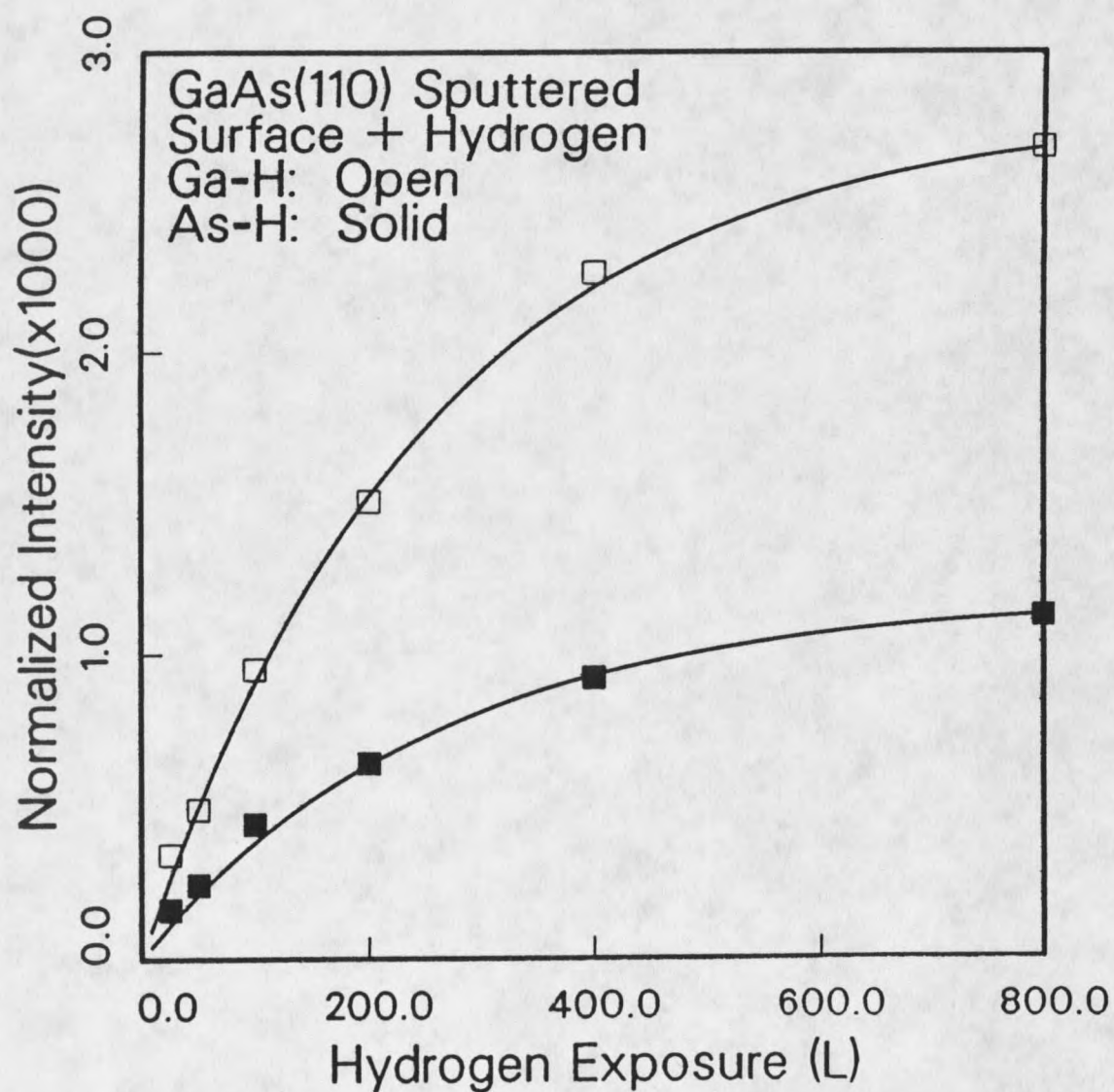


Fig.24

The H uptake behavior for the sputtered GaAs(110) surface. The Ga-H (open squares) and the As-H (solid squares) stretch intensities are plotted as a function of H exposure (L). The full lines are predicted from a model fitting.

exposure to that at saturation coverage of 400 L, the coverage of the first H exposure is about 16% of a monolayer, which suggests several properties of the initial adsorption stage.

First, in the initial stage the H has not degraded the surface atomic structure by desorbing As as AsH_2 or AsH_3 as it does in the dissociation stage described in Ref 50. The following evidences support the idea. From the H uptake curve shown in Figure 23, we monitored the adsorption starting from low coverage extending up to saturation; the dissociation stage⁵⁰ would occur for much higher H exposure. The HREELS elastic peak intensity does not decrease much, which also implies that the surface atomic order is sufficient to produce a well defined reflected elastic beam. Furthermore, the LEED pattern shows only a slight increase of the background, which indicates that the surface atomic structure is not disrupted severely. Finally the XPS data (to be presented later in detail) show that the As loss is minimal.

Second, in the initial adsorption stage the adatom-adatom interaction is small and the substrate perturbations due to H adsorption do not overlap. In fact, the smooth monotonic behavior of the uptake curve suggests that the adatom-adatom interaction is not strong even for high coverage. One would expect that hydrogen only perturbs a small part of the substrate near the adsorption site, since the H atom is quite small. Theoretical calculations⁶³ have shown that the adatom-adatom interaction is indeed weak for H adsorption on the GaAs(110) surface. Kahn has discussed the relaxation stability of this surface⁴⁵ and concluded that GaAs(110) surfaces prepared by thermal decomposition with a large anion deficiency have LEED I-V profiles identical to those measured for the one-to-one stoichiometric surfaces. A similar behavior is found for column III metal atoms adsorbed on GaAs(110) where excess surface cations form metallic islands or clusters which do not perturb the relaxed surface in areas where stoichiometry is maintained.

The hydrogen uptake behavior shown in Figures 23 and 24 can be modeled with the use of the following consideration. Let θ denote the coverage, L the H exposure, and $\Delta\theta$ and ΔL the variations of coverage and exposure. To the first approximation, the increase of the coverage $\Delta\theta$ should be proportional to the exposure increment and to the clean surface area. Mathematically,

$$\Delta\theta = A\Delta L(1-\theta) . \quad (6.1)$$

Eq. (6.1) can be integrated to obtain

$$\theta = 1 - \exp(L/L_0) \quad (6.2)$$

where $L_0 = A^{-1}$, a constant determined by the sticking coefficient, the atomic hydrogen generating rate, and the geometrical set-up of the exposure. Thus, L_0 will be different from surface to surface. The intensity of the stretch is then

$$I = I_s \theta = I_s [1 - \exp(L/L_0)] \quad (6.3)$$

where I_s is the intensity at saturation coverage. By adjustment of I_s and L_0 , the uptake curves are fitted as shown in Figures 23 and 24 by the full lines. The fit for the Ga-H and As-H lines on the cleaved surface gives for I_s the values of 7.3×10^{-5} and 2.5×10^{-5} , respectively. The value of L_0 is 83 L and is constrained in the fit to be the same for the Ga-H and the As-H stretch intensities. Without knowing the absolute atomic hydrogen exposure, the value of L_0 cannot be used to determine any physical properties of the adsorption process. Therefore, the value of L_0 will not be quoted in latter text.

As discussed in Chapter 3, the vibrational intensity can be calculated within the dipole scattering regime. Using Eq. (3.13) and the estimated analyzer full acceptance angle of 2° , We calculate the effective charges of the Ga-H and the As-H stretch modes to be 0.036 e and 0.025 e, respectively, where e denotes the electronic charge. In calculating the charge, the areal density of adsorbed hydrogen, n_s , and the intensity of the HREELS stretch line corresponding to n_s are needed. It is assumed that at saturation, the coverage is one hydrogen per surface atom and the intensity is I_s , the asymptotic fitting value of the model. The density n_s can be calculated with the lattice constant of GaAs.

For the sputtered surfaces, the results are similar in that hydrogen adsorbs to both the surface Ga and As atoms. The fit for the model is shown in Figure 24 by the full lines. The values of I_s for Ga-H and As-H stretch modes are 2.8×10^{-3} and 1.2×10^{-3} , respectively. The ratio of the As-H intensity to the Ga-H intensity is 0.43, which is slightly larger than that of the cleaved surface. This point is discussed in more detail later.

The effective charge of the H-substrate bonds for the sputtered surface cannot be calculated with Eq. (3.13). On a disordered surface, there is no well-defined specular direction; thus the scattering cross section formula discussed in Chapter 3 is not applicable. The signal in the specular direction may have large contribution from the impact scattering since the reflected beam diverges into a very large solid angle. Experimentally one can observe that the elastic peak intensity does not change much when the analyzer is moved by $5\text{-}10^\circ$. Therefore, the normalized absolute intensity of the stretch modes cannot be used to derive the effective charge. However, the intensities of the Ga-H and As-H bonds are useful when they are compared to each other. Such a ratio reveals the difference in their effective charge and the number of adsorbed H atoms on the surface.

To monitor the surface composition, XPS intensities of the Ga 2p (365 eV kinetic energy) and the As 2p (169 eV kinetic energy) lines were taken for the clean cleaved surface, for the surface with saturated hydrogen exposure, and for the sputtered surface. The ratio of the two lines remains essentially the same for the three cases. Since both peaks are surface sensitive, we conclude that there is no significant change for the surface stoichiometry and the loss of As through AsH_3 is very small.

The LEED patterns were examined visually. After saturation with hydrogen, the background was slightly higher, while the spot sharpness remained comparable with that of the clean surface. These observations suggest that some random disorder has occurred on the surface. The effect is consistent with a small reduction of the HREELS elastic peak intensity after hydrogen saturation.

To summarize, the atomic hydrogen is observed to adsorb on both the Ga and As surface atoms via their dangling bonds; that is, no preferential adsorption occurs for any hydrogen coverages ranging from 16% of a monolayer to saturation. The effective charge for the Ga-H and the As-H bonds is calculated as 0.036 e and 0.025 e, respectively; and essentially no stoichiometric changes nor surface disordering are observed. Hydrogen chemisorption on the sputtered surface behaves similarly.

Gallium Phosphide

The HREELS spectra for the cleaved surface and that with chemisorbed hydrogen are shown in Figure 25.⁶⁴ The loss peak at 48 meV, accompanied by three overtones, is attributed to the Fuchs-Kliwer optical phonon.⁵⁸ No trace of a plasmon loss was detected. The intensity ratio of the fundamental phonon to the

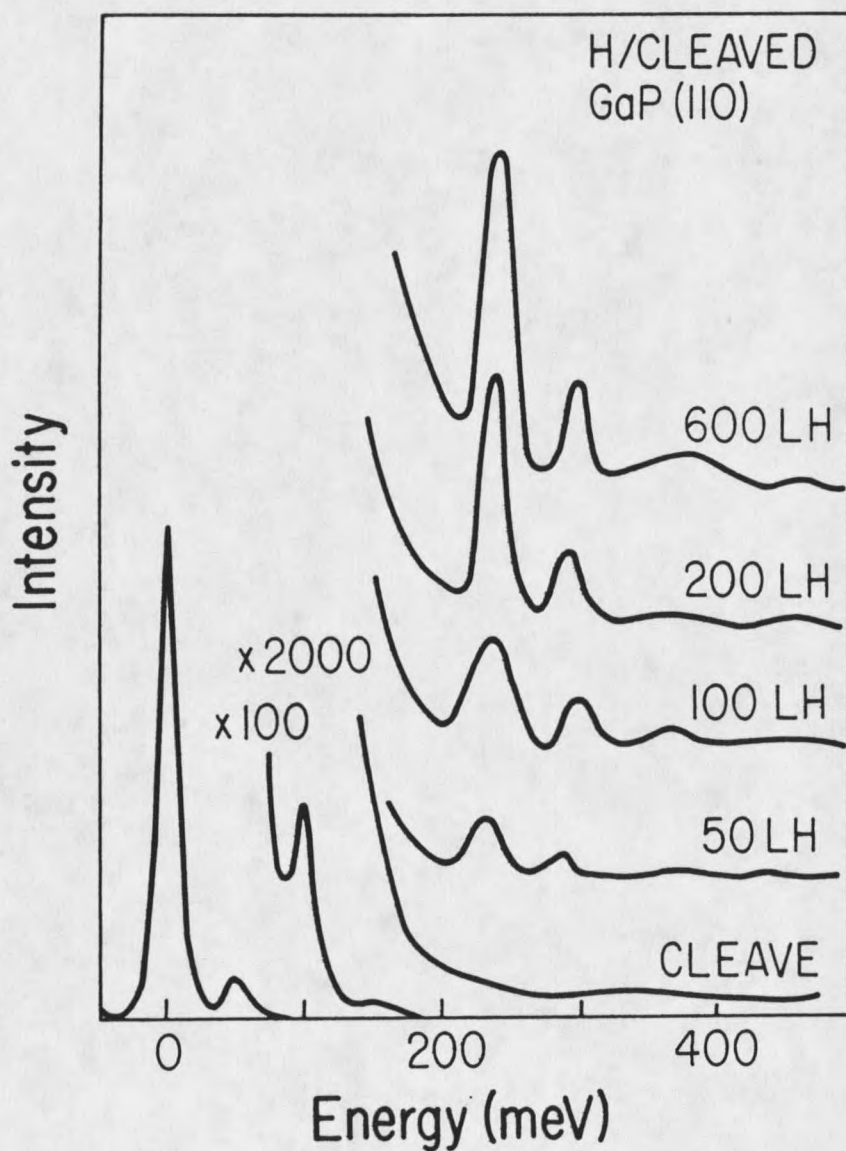


Fig.25

The HREELS spectra for cleaved and H chemisorbed GaP(110) surfaces. The two losses at 231 and 291 meV are the Ga-H and the P-H stretches, respectively. The primary beam energy is 11 eV and the angle of incidence is 45° .

elastic peak is about 0.14. The position and intensity of the phonon line show no dependence on H adsorption. The spectra for the H-exposed surface show two loss lines at 232 and 288 meV, which are attributed to Ga-H and P-H stretch modes, respectively. At the initial exposures, the ratio of the P-H stretch intensity to that of the Ga-H stretch is 0.4. As the H-exposure increases, the ratio continuously decreases to 0.3 at saturation coverage; this could suggest the loss of surface P atoms. Note that these ratios are much larger than that of the phonon to the elastic peak, and accordingly the 288 meV peak should not be interpreted as the combination loss of the 232 meV Ga-H stretch and the 48 meV optical phonon. The H-uptake behavior for the cleaved surface is shown in Figure 26, where the open squares are the Ga-H stretch, the filled squares are the P-H stretch, and the full lines are the model fits. The value of I_s for Ga-H and P-H is 3.6×10^{-4} and 1.1×10^{-4} , respectively. As found for the GaAs case, no preferential adsorption is observed throughout the exposure range, although the P-H intensity becomes smaller relative to the Ga-H intensity as the hydrogen coverage increases, a result which could be due to the P desorption. Substituting the experimental parameters into Eq. (3.13), the effective charges for the Ga-H and the P-H bonds are found to be 0.086 e and 0.060 e, respectively. Note that the values are both larger in comparison to those obtained for Ga-H and As-H stretch modes on GaAs.

Spectra for the sputtered surfaces are shown in Figure 27. It is seen that hydrogen adsorbs at both the surface cation and anion site, whereas the relative intensity ratio of the anion-H and cation-H loss lines is enhanced by about a factor of two in comparison to that of the cleaved surface. The uptake data and model fits are shown in Figure 28. The value of I_s for Ga-H and P-H stretch modes is 3.3×10^{-3} and 1.9×10^{-3} , respectively.

The XPS core lines measurement shows, for saturated hydrogen exposure, about

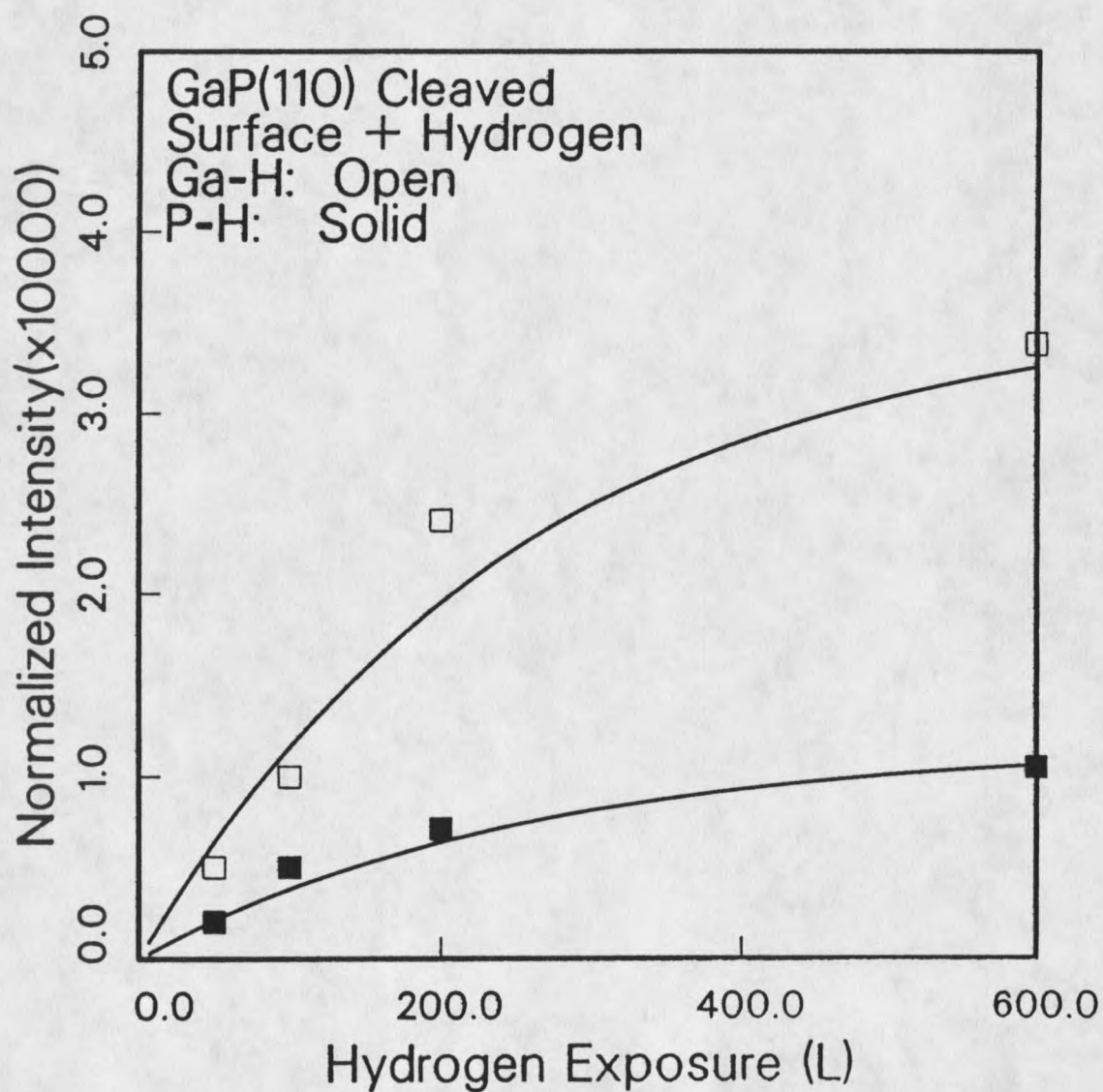


Fig.26

The H uptake behavior for the cleaved GaP(110) surface. The Ga-H (open squares) and the P-H (solid squares) stretch intensities are plotted as a function of H exposure (L). The full lines are predicted from a model fitting.

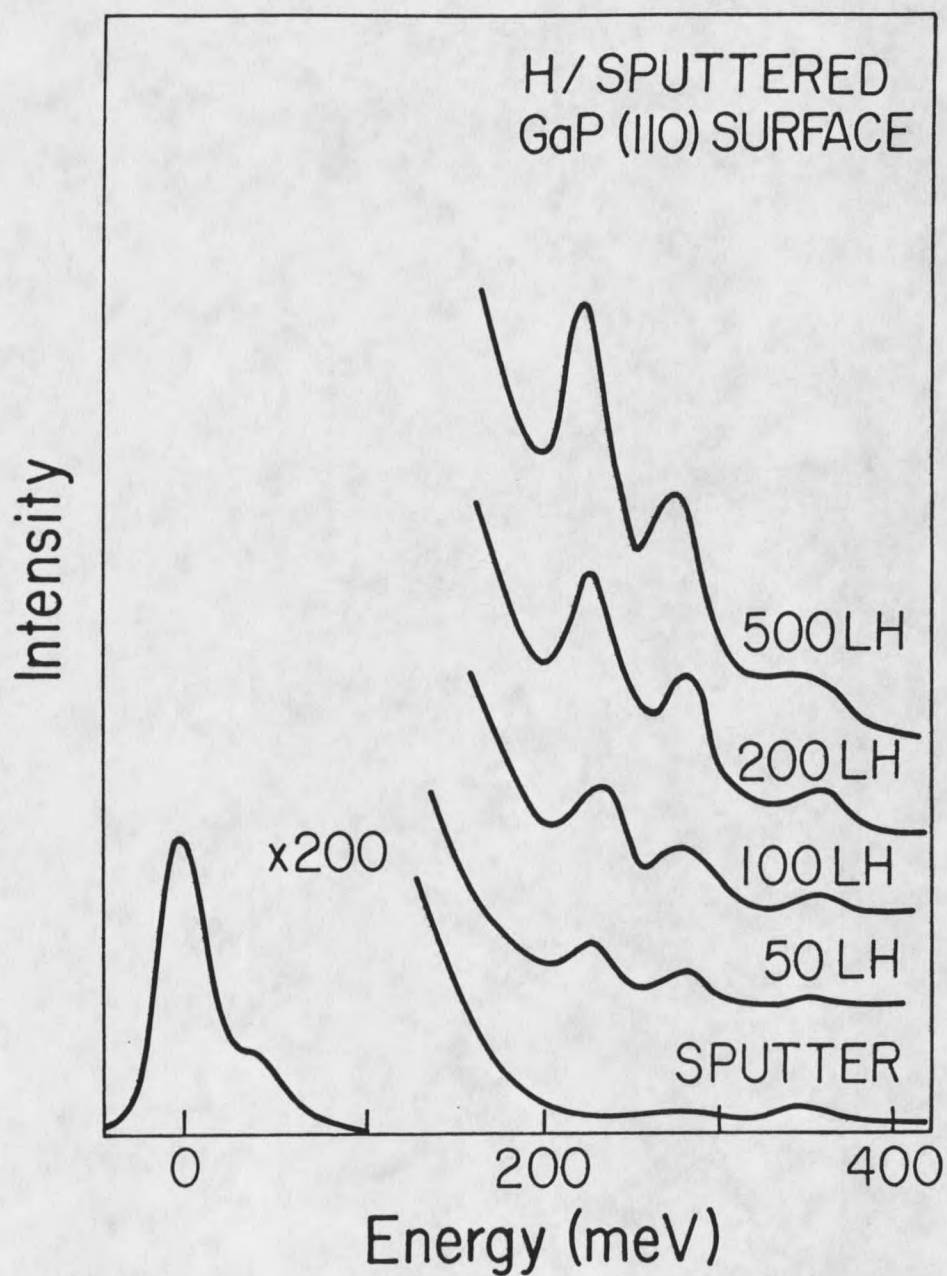


Fig.27

The HREELS spectra for sputtered and subsequently H-exposed the GaP(110) surfaces. The primary beam energy is 4 eV and angle of incidence is 60°.

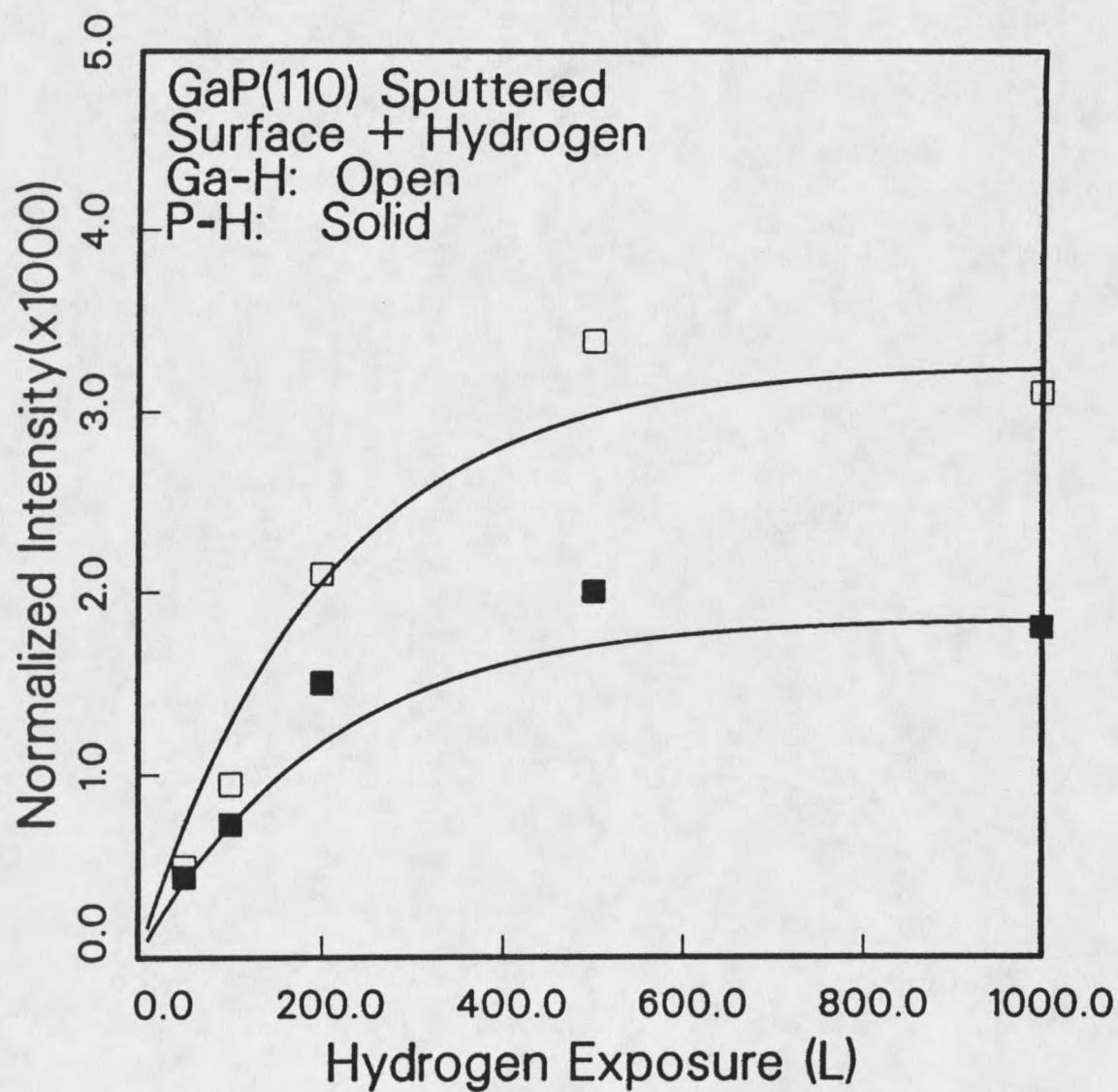


Fig.28

The H uptake behavior for the sputtered GaP(110) surface. The Ga-H (open squares) and the P-H (solid squares) stretch intensities are plotted as a function of H exposure (L). The full lines are predicted from a model fitting.

a 20% reduction in the P Auger (122 eV) to the Ga 2p (369 eV) ratio, compared with that of clean surface. The reduction indicates the loss of P during hydrogen adsorption, which is consistent with the decrease of the relative intensity ratio of P-H and Ga-H for the HREELS results. After light sputtering of the surface, the same XPS core lines ratio shows a 20% reduction in comparison to that of clean surface. However, in contrast to the anion deficiency caused by sputtering, the anion-H stretch intensity is relatively enhanced. The enhancement of the anion-H stretch indicates that the preferential removal of surface atoms is not the only consequence of the sputtering; changes in the chemical properties also occur.

Indium Phosphine

Hydrogen chemisorption on the InP(110) surface has been studied by Schaefer *et al.*^{59,60} In their experiments, the hydrogen exposure was made with the sample out of the line of sight of the tungsten filament used for H dissociation. The observations were used to conclude that on the cleaved InP(110) surface there is a preference for adsorption on the In sites at the initial stage, whereas on the sputtered surface the P is the preferred site. In their hydrogen coverage study the first coverage measured was estimated at about a quarter of a monolayer. In our setup, the H exposure was made with the sample in the line of sight of the filament and the results show some differences. The loss spectra for the cleaved and sputtered surface are shown in Figures 29. The uptake data for the cleaved surface are shown in Figure 30. The I_s value for In-H and P-H stretch modes obtained from model fitting are 5.0×10^{-4} and 1.0×10^{-4} , respectively. The uptake data for sputtered surface are shown in Figure 31. The I_s value for In-H and P-H stretch modes is 1.0×10^{-3} and 8.0×10^{-3} , respectively. The first H coverage obtained for the cleavage

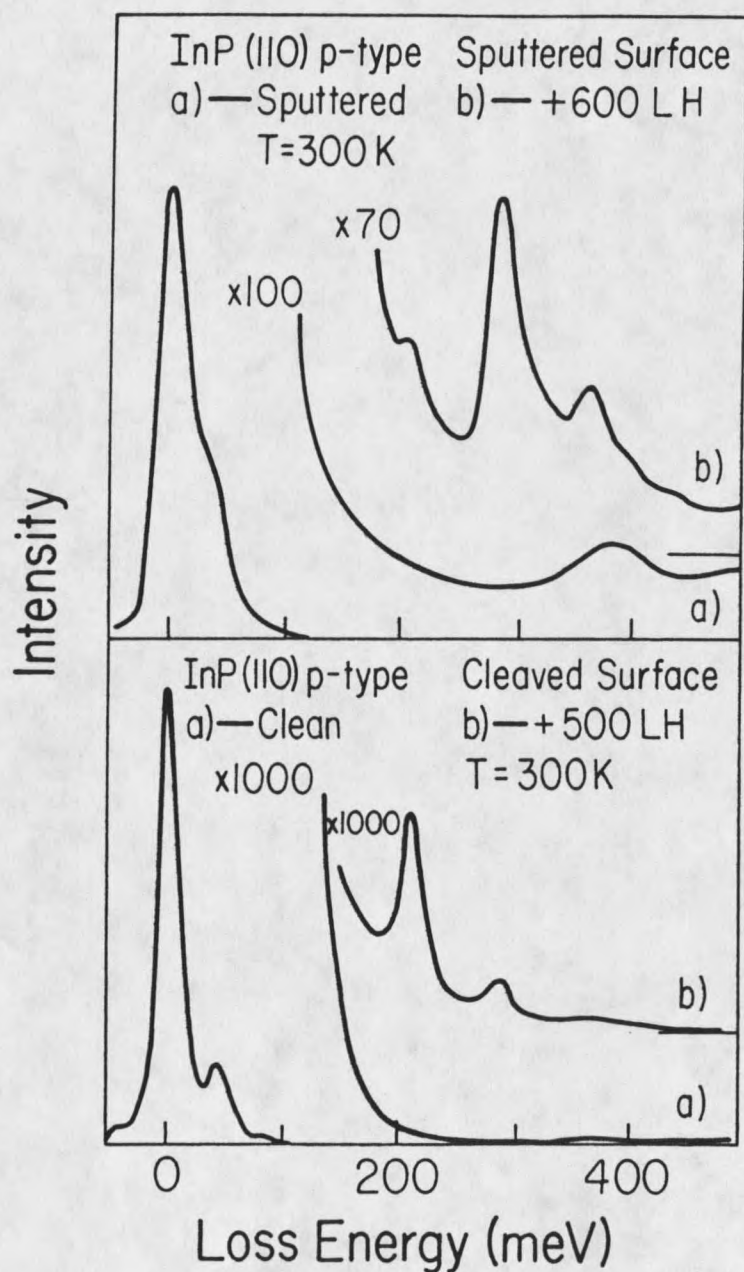


Fig.29

The HREELS spectra of InP(110) surfaces. Lower panel curve a) is as cleaved and curve b) is after 500 L H exposure. Upper panel curve a) is sputtered surface and curve b) is after 600 L H exposure. The primary beam energy is 6.7 eV and the angle of incidence is 45° .

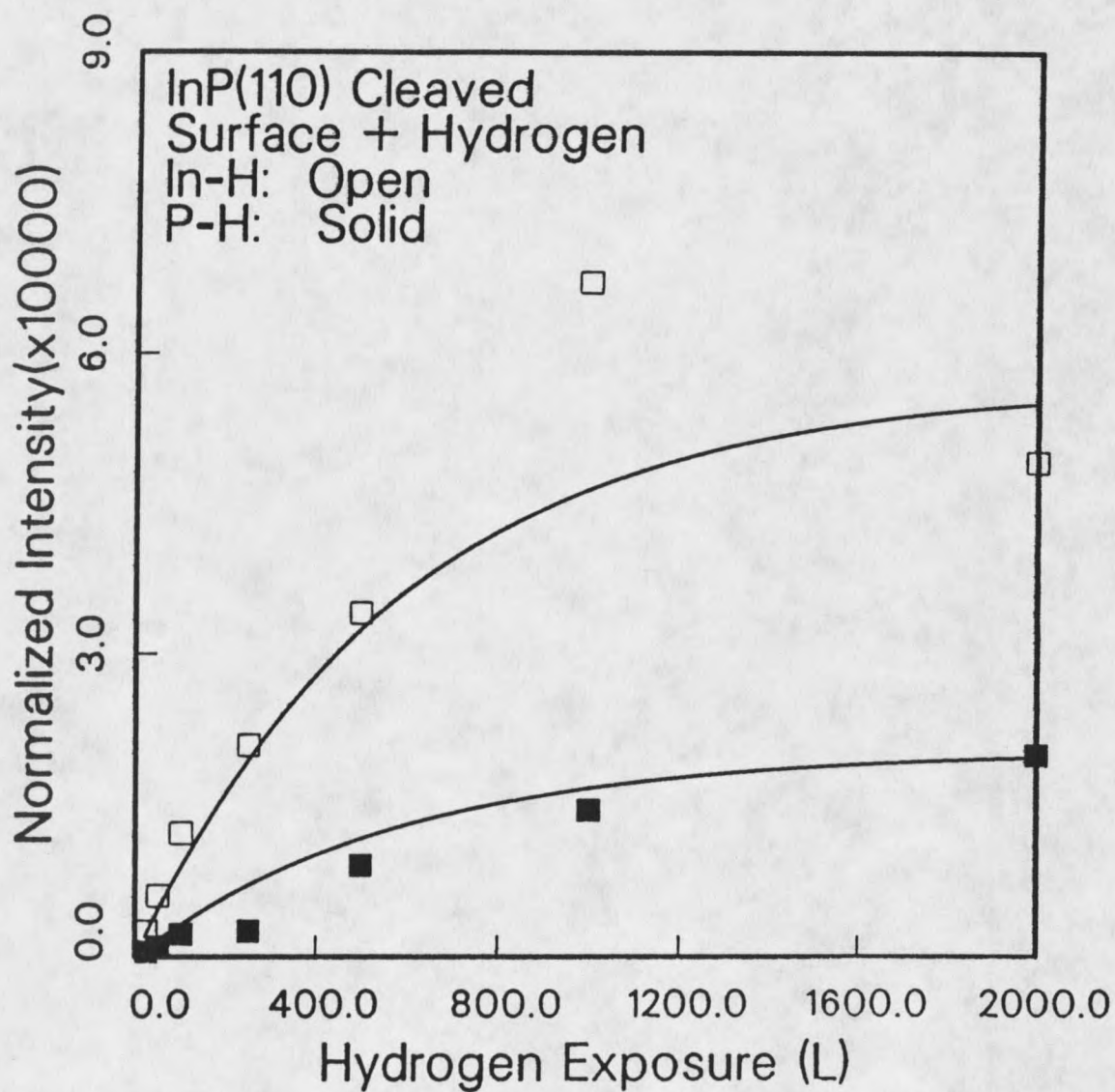


Fig.30

The H uptake behavior for the cleaved InP(110) surface. The In-H (open squares) and the P-H (solid squares) stretch intensities are plotted as a function of H exposure (L). The full lines are predicted from a model fitting.

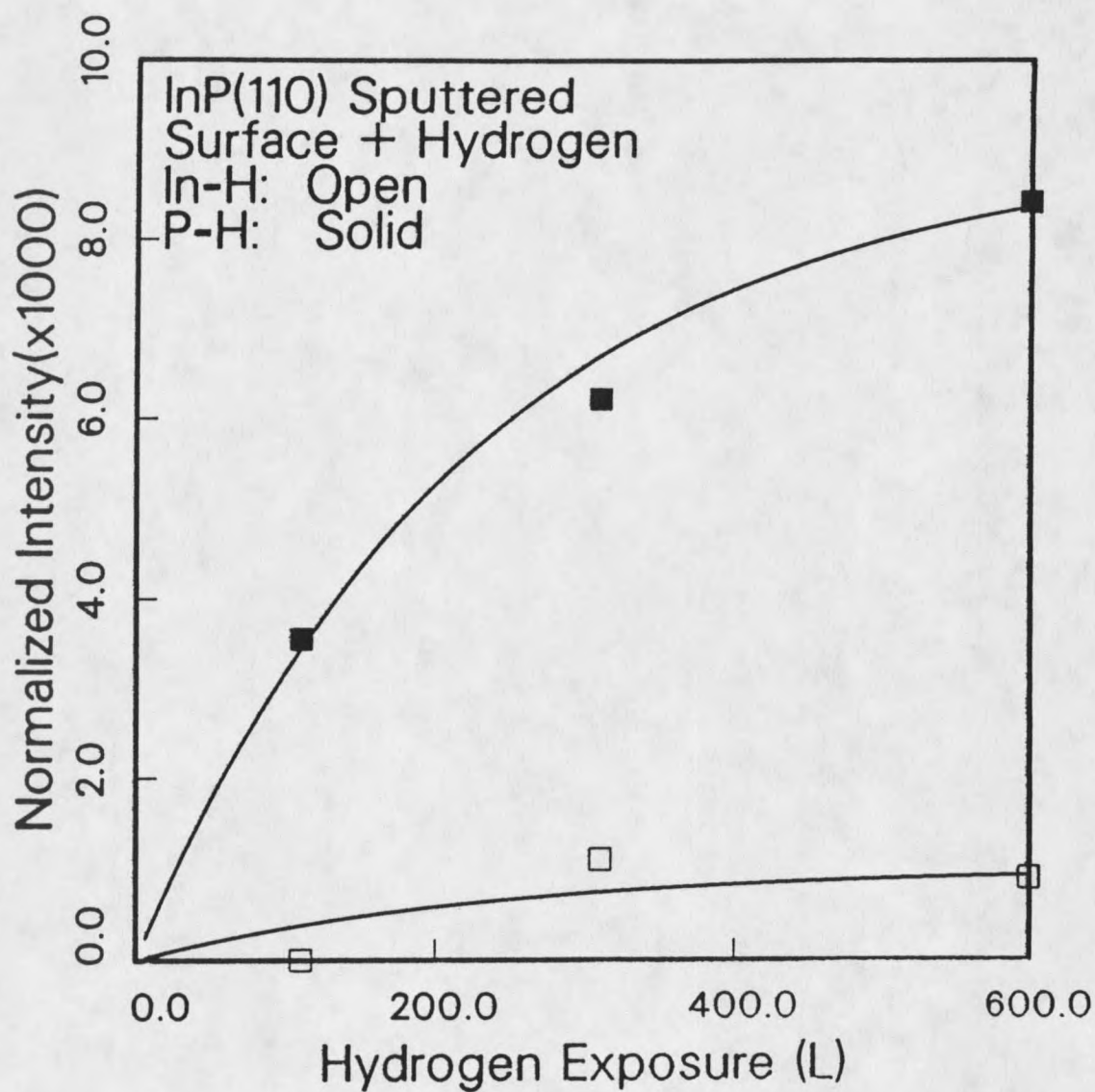


Fig.31

The H uptake behavior for the sputtered InP(110) surface. The In-H (open squares) and the P-H (solid squares) stretch intensities are plotted as a function of H exposure (L). The full lines are predicted from a model fitting.

surface is about 4-5% of a monolayer coverage. This coverage is much smaller than that of Schaefer *et al.*,⁶⁰ but stretch vibrations corresponding to both In-H and P-H are present. Throughout the exposure range, the ratio of the P-H intensity and the In-H intensity is roughly a constant at about 0.2 although the data scattered; The strong P-H stretch intensity argues against the preferential adsorption model. The effective charges calculated with Eq. (3.13) are 0.11 e for In-H and 0.072 e for P-H. Note that the effective charge for P-H is 60% of that of In-H, which is much larger than the stretch intensity ratio of 0.2. The difference in the intensity ratio is implied in Eq. (3.13), where the loss peak intensity is inversely proportional to the loss energy and directly proportional to the square of the effective charge. Thus, the small intensity losses at high loss energy should be carefully measured with enough statistics to be adequately analyzed.

For the sputtered surface, the P-H intensity is enhanced by a factor of 40 relative to In-H, as compared to the values for the cleaved surface. This phenomenon indicates that the chemical properties are altered dramatically by sputtering.

Gallium Antimonide

The GaSb(110) cleaved surface behaves differently than those of GaAs, GaP and InP in terms of the kinetics of the hydrogen adsorption at room temperature. For exposures up to 5000 L H no adsorption is observed. However, the elastic peak intensity decreases after hydrogen exposure, indicating that hydrogen is changing the surface. When the sample was cooled down to 80 K, a loss at 230 meV was observed, as indicated in Figure 32. It is not possible to determine whether this loss is due to Ga-H or Sb-H stretch modes, since their stretch frequencies are

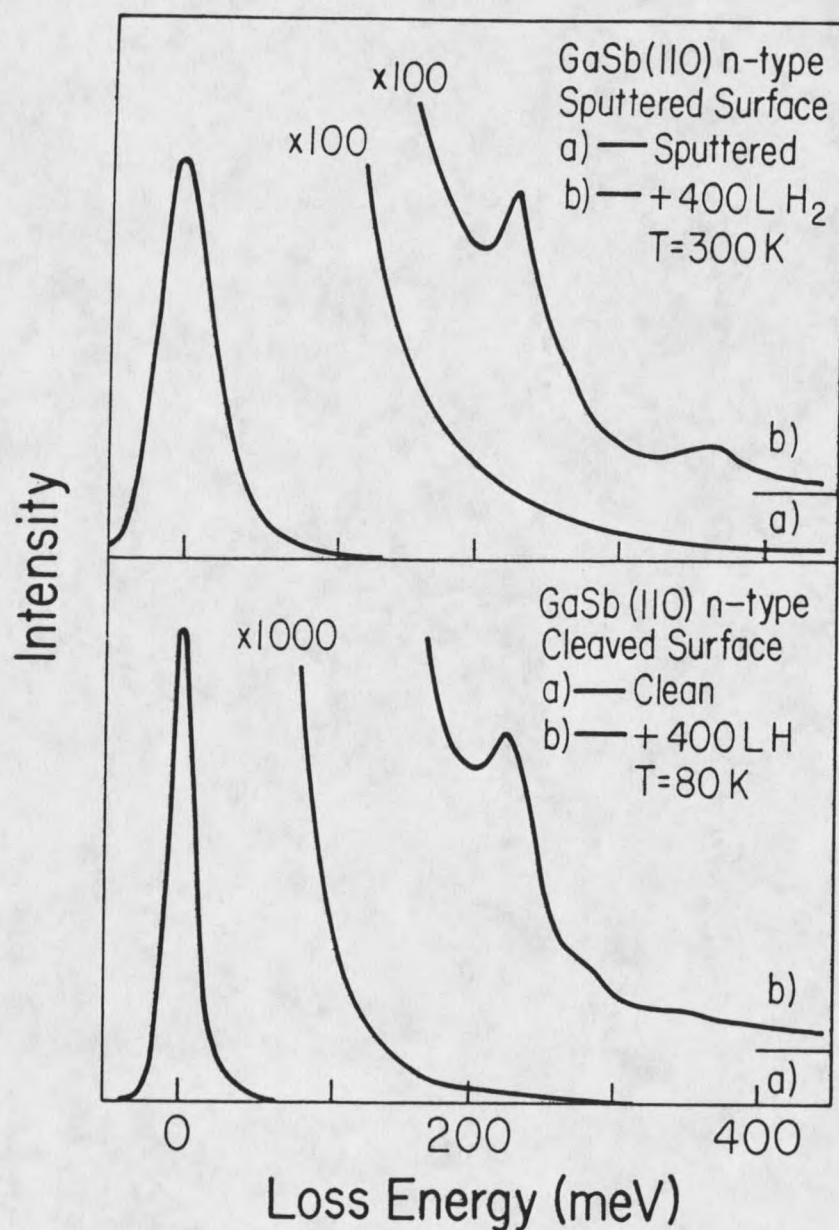


Fig.32

The HREELS spectra for GaSb(110) surface. Lower panel curve a) is as cleaved and curve b) is after 400 L H exposure. Upper panel curve a) is sputtered surface and curve b) is after 400 H exposure. The primary beam energy is 6.5 eV and the angle of incidence is 60°. The cleaved surface and its hydrogen exposed spectra were taken at 80 K.

very close. From the strong intensity it is suggested that both vibrational modes contribute.

For the sputtered surface, spectra of which are shown in Figure 32, H adsorption occurs at room temperature with a loss at 230 meV indicating a dramatic change, due to sputtering, of the adsorption kinetics. Species identification is still not possible in this case.

The ratio of the XPS core lines for the Sb Auger line (464 eV) and the Ga 2p line (369 eV) indicates no stoichiometry change after the cleaved surface is exposed to 4000 L H, whereas this ratio decreased about 10% for sputtered surfaces with a subsequent 1000 L H exposure.

Indium Antimonide

Hydrogen adsorption does not occur at room temperature for either the cleaved (up to 2000 L) or sputtered (up to 1100 L) InSb surfaces, in disagreement with the results reported by Hinkel *et al.*⁶² At 80 K, losses at 208 and 230 meV were observed for the cleaved surface with the hydrogen exposure as noted in Figure 33. The 230 meV peak can be assigned to the Sb-H stretch. The interpretation of the loss at 208 meV presents some ambiguities because the In-H stretch and water scissor modes both occur in this region. The In-H stretch frequency is around 215 meV on the InP(110) surface and 216 meV on the sputter-annealed InSb(111) surface⁶¹, which are at considerably larger energies than 208 meV observed in our data. On the other hand, the presence of water is evidenced by the broad structure around 420-450 meV in the spectra. It is known that the H-O-H stretch of water has a mode at 420 meV and the scissors mode is at 205 meV.⁶⁵ However, the intensity of the scissor mode is weaker in Ref. 65 than the 208 meV peak in our

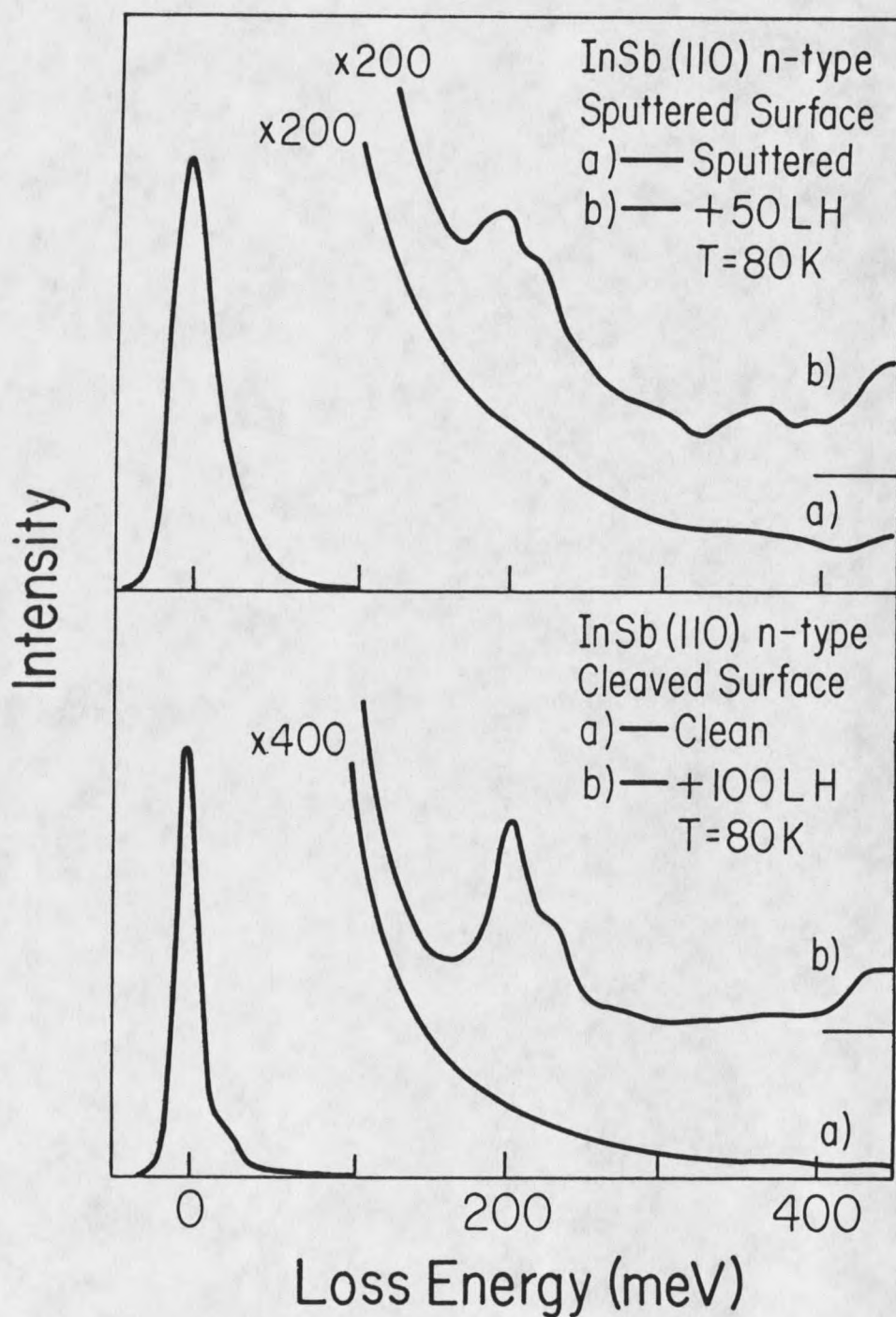


Fig.33

The HREELS spectra for H adsorption on InSb(110) surface. Lower panel curve a) is as cleaved and curve b) is after 100 L H exposure. Upper panel curve a) is sputtered surface and curve b) is after 50 L H exposure. All spectra were taken at 80 K with a primary energy of 4 eV and an angle of incidence of 60° .

data if the 420-450 meV intensity is used as an amplitude reference. To verify that the spectral features are due to water, a deliberate water exposure of 0.1 L was made for a InSb(110) cleaved surface at 80 K. The spectrum obtained for the exposure is shown in Figure 34. One notices that the water scissor mode is indeed weak. In addition, the 208 meV peak in Figure 33 disappears because of thermal desorption when the temperature is raised to about 140 K, whereas the water peak near 450 meV remains unchanged. Thus we conclude that the In-H stretch makes a significant contribution to the 208 meV loss peak.

It is evident that hydrogen adsorption at low temperature also drastically degrades the surface order, since the elastic peak intensity is substantially decreased after hydrogen exposure. This result is in contrast to observations made after room temperature H exposure on the same surface, where the elastic peak intensity was essentially unchanged.

For the sputtered surface, both the In-H and Sb-H losses shift down in energy and the former is enhanced relative to the latter (see Figure 34). However, the presence of the water scissor mode makes it impossible to draw quantitative conclusions.

Indium Arsenide

The HREELS spectrum for H adsorption at 120 K on the InAs(110) cleaved surface at is shown in Figure 35 along with that of the freshly cleaved surface. For the clean surface, the Fuchs-Kliwer phonon is at 30 meV.

After the surface is dosed by 500 L H exposure at 120 K, the phonon and plasmon in the accumulation layer form two coupled modes which appear in the low energy loss region. In Chapter 5 these modes are discussed in detail. Because of

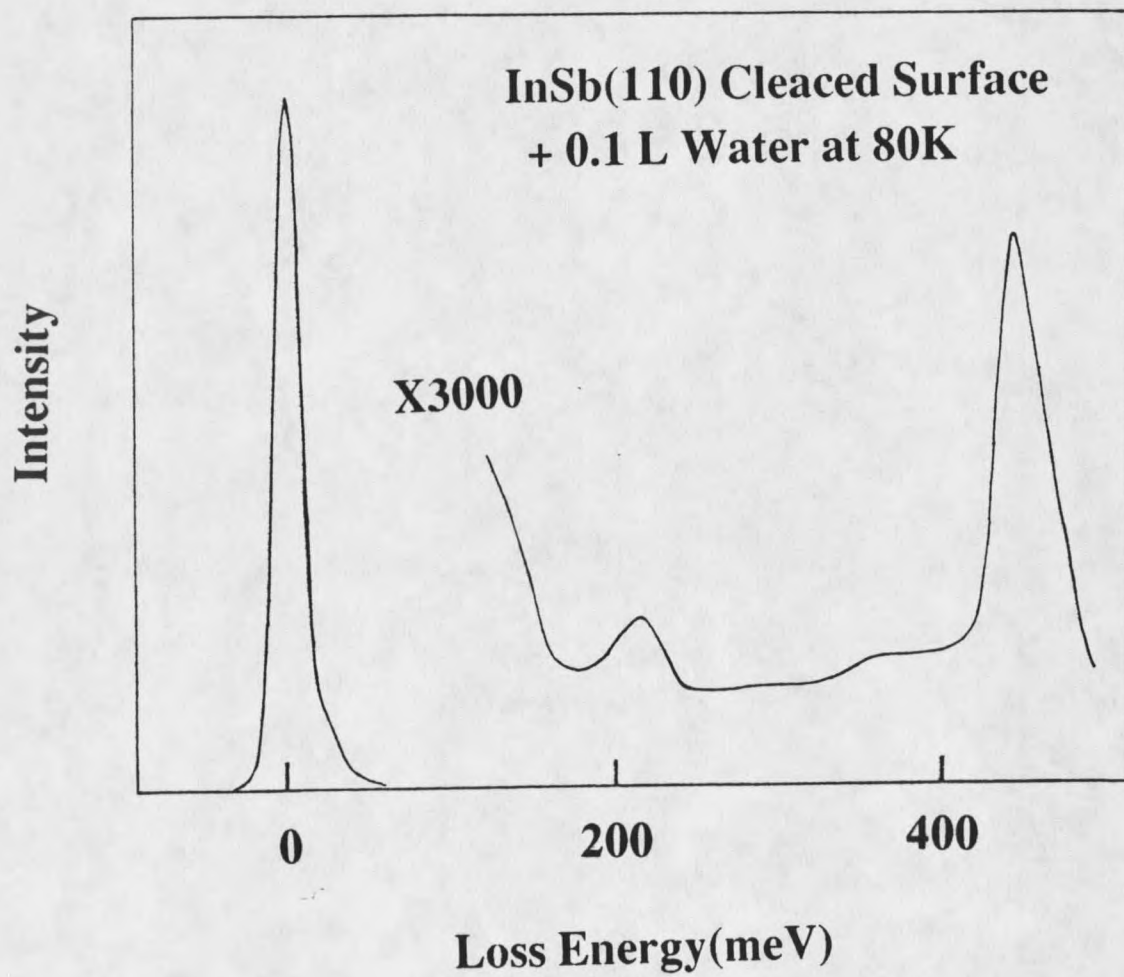


Fig.34

The HREELS spectrum for the cleaved InSb(110) surface after 0.1 L water exposure at 80 K.

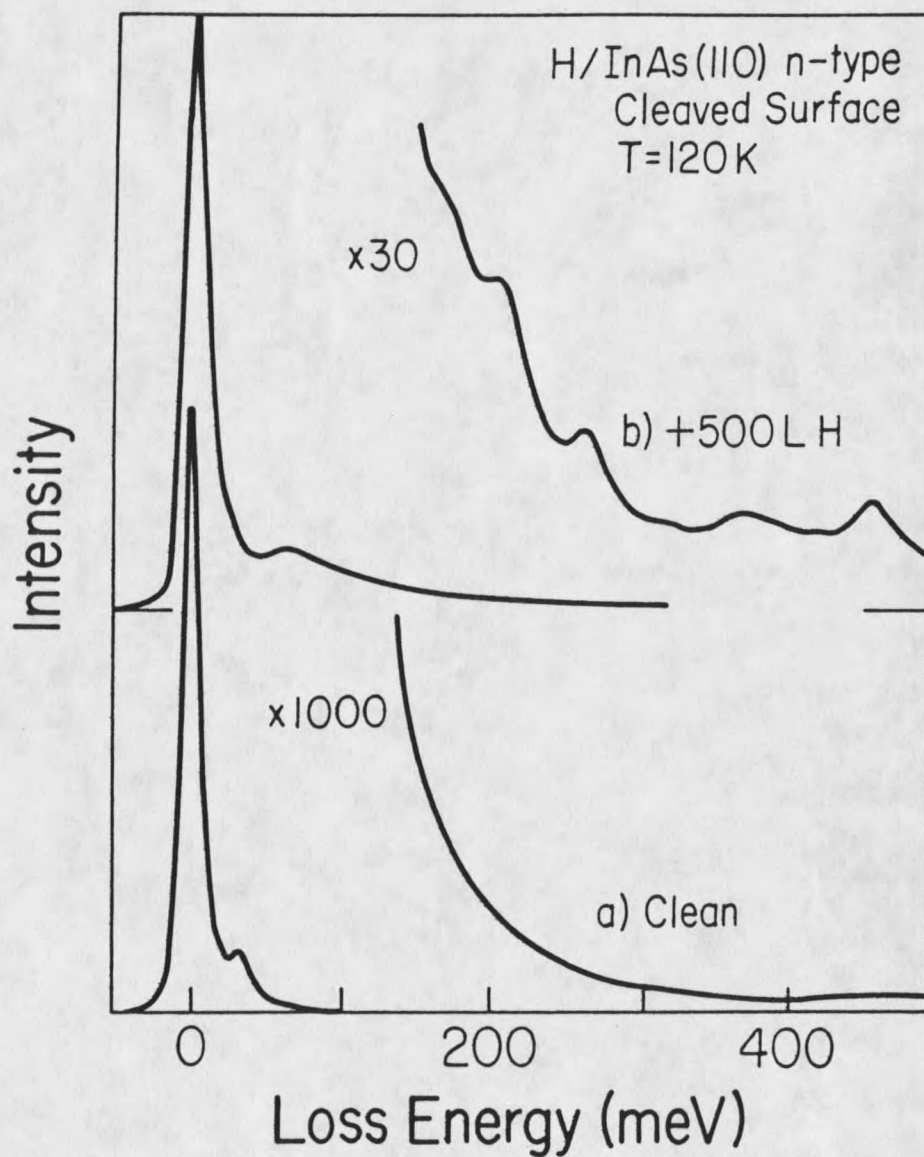


Fig.35

The spectra for cleaved InAs(110) surface. Curve a) is as cleaved and curve is after 500 L H exposure. The primary beam energy is 11 eV and the angle of incidence is 45° .

the very high background due to these modes, it is impossible to study the initial stages of the H adsorption. A very large hydrogen exposure is needed to actually observe the H-substrate stretch modes, but the high exposure degrades the surface order dramatically. The degradation is evidenced by a reduction at least a factor of 30 of the elastic peak intensity.

The loss at 260 meV seen in Figure 35 is due to the As-H, stretch while the loss at 360 meV is due to the C-H stretch. The structure around 450 meV is due to the O-H stretch, which could come from either the water or the hydroxyl group. The loss at 200 meV cannot be uniquely attributed to the In-H stretch because it is close to the energy of the scissors mode of water.⁶¹ At room temperature no stretch lines due to H adsorption were observed up to H exposure of 1.2×10^4 L. Nevertheless hydrogen exposure does change the surface, e.g., an accumulation layer forms, the elastic peak intensity is reduced by a factor of two, and a higher LEED background is observed.

Adsorption of hydrogen on a sputtered InAs(110) surface occurs at room temperature, and the spectrum obtained for the sputtered sample is shown in Figure 36. For the sputtered surface, a strong loss at 360 meV due to C-H is present, in addition to the plasmon which dominates the lower energy part of the spectrum. The C-H is believed to be caused by the ion-gun used in the sputtering. The filament in the ion gun is homemade from a tungsten wire which may contain a high concentration of carbon. After hydrogen exposure of 200 L, a loss at 260 meV is resolved which is readily assigned to the As-H stretch, whereas no feature is present to assign to the In-H stretch.

The effects of H adsorption were monitored by observation of the XPS lines of As 2p (165 eV) and In Auger (820 eV). Compared with the clean cleaved surface, the ratio of these two lines increased 8% for the surface after H adsorption and

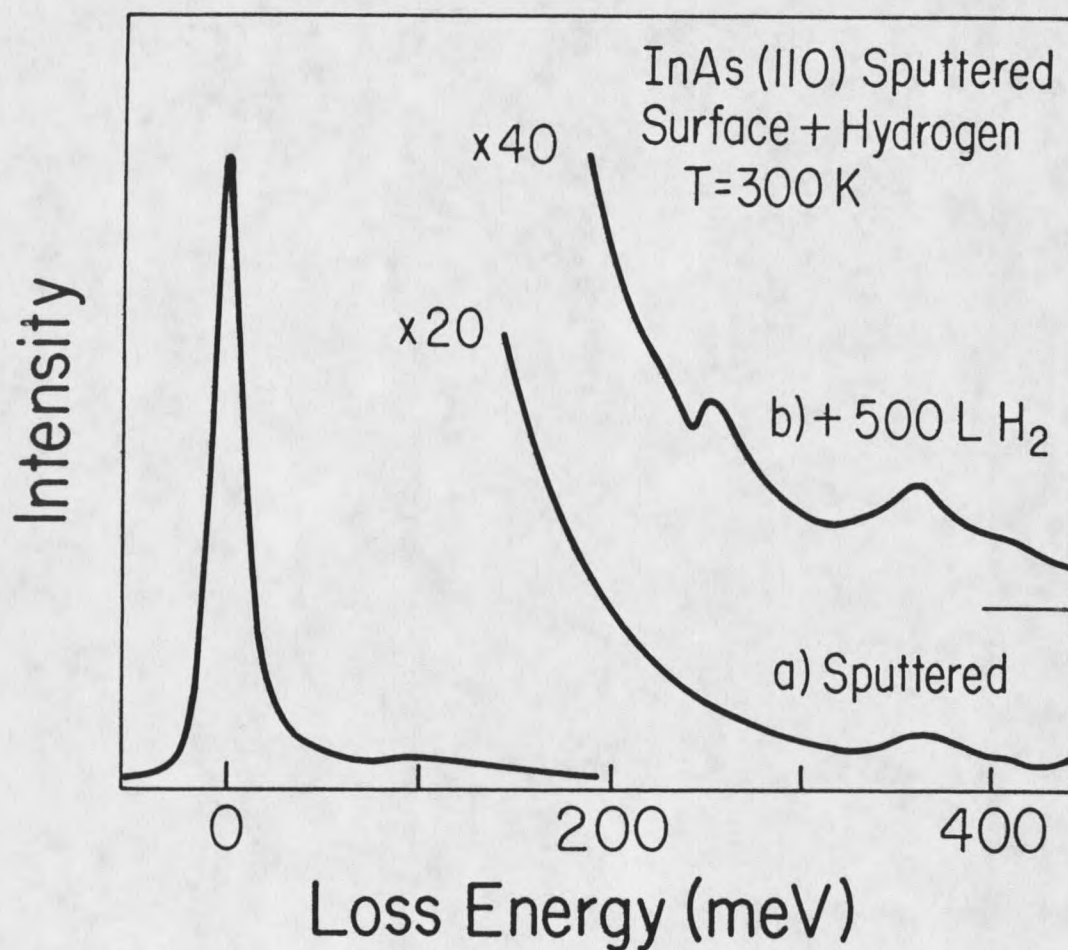


Fig.36

The spectra for sputtered InAs(110) surface. Curve a) is sputtered surface and curve b) is after 500 L H exposure. The spectra were taken at room temperature with a primary beam energy of 11 eV and an angle of incidence of 45°.

decreased 25% for the sputtered surface with subsequent H exposure of 2000 L.

Summary of Experimental Results

Table 2 lists the stretch frequencies, normalized intensities, intensity ratios of anion-H and cation-H stretch modes and the calculated effective charges for the cleaved surface. The common features of the results for each crystal are: a) H bonds to both the cation and the anion surface dangling bonds of the cleaved surface; b) no preferential adsorption occurs; c) perturbations due to stoichiometry changes on the surface after H chemisorption are not significant.

Table 2 Summary of the results on cleaved surfaces. The stretch frequency is in meV, the effective charge is in unit of electron charge e , and I_s is the normalized intensity of H-substrate stretch obtained from model fitting.

<u>Cleaved Surface</u>	GaAs	GaP	InP	GaSb	InSb	InAs
Stretch frequency						
Cation-H	231	232	212	228	200	205
Anion-H	262	288	288		229	260
Intensity I_s						
Cation-H	7.3×10^{-5}	3.6×10^{-4}	5×10^{-4}	7×10^{-4}	9×10^{-4}	2×10^{-3}
Anion-H	2.5×10^{-5}	1.1×10^{-4}	1×10^{-4}		4×10^{-4}	2×10^{-3}
Average Ratio	0.34	0.31	0.2		0.44	1.0
Effective charge						
Cation-H	0.036	0.086	0.11		0.126	
Anion-H	0.025	0.060	0.072		0.097	

Table 3 summarizes the results of hydrogen chemisorption on sputtered surfaces of these compound semiconductors. For sputtered surfaces the common features are: a) light sputtering of the cleaved surface causes drastic changes in the adsorption behavior, generally resulting in enhancement of the anion-H stretch intensity; b) changes in the surface stoichiometry after sputtering are insignificant and in particular are not responsible for the enhancement of the anion-H stretch intensity.

Table 3 Summary of the results on sputtered surface. The stretch frequency is in meV, I_s is the normalized intensity of H-substrate stretch obtained from fitting.

<u>Sputtered surface</u>	GaAs	GaP	InP	GaSb	InSb	InAs
Stretch Frequency						
Cation-H	231	231	210	232	197	
Anion-H	260	287	288		221	
Intensity I_s						
Cation-H	2.8×10^{-3}	3.3×10^{-3}	1×10^{-3}	4×10^{-3}	1×10^{-3}	
Anion-H	1.2×10^{-3}	1.9×10^{-3}	8×10^{-3}		7×10^{-4}	
Average Ratio	0.43	0.7	8.0		0.7	

Analysis and Discussion

The Effective Charge and Loss intensity

In studying the chemisorption of simple molecules on semiconductor surfaces,

many workers have used HREELS data to identify chemisorption species or adsorption sites. However, less effort has been extended to utilize the absolute loss-line intensity for studying adsorbate behavior. In infrared and Raman spectroscopic studies, analysis of the vibration intensities has proved a rich source of information.⁶⁶ In this section, the intensities of the loss lines are examined.

A chemisorbed species, the H atom in our case, usually donates or receives charge from the substrate atoms when a chemical bond forms. The charge transferred can be positive or negative depending on the relative electronegativity of adsorbate and substrate atoms. Because of the charge transfer a dipole moment is formed on the surface. The dipole moment can be expressed as

$$\mu = 2e^*q \quad (6.4)$$

where e^* is the charge transfer, q is the distance between adsorbate and substrate and the factor 2 arises from the image effect. The dipole interaction potential in the presence of an external electric field E is given by

$$V_{\text{int}} = \mu E \quad (6.5)$$

The force exerted on the dipole is given by

$$F = \frac{\partial}{\partial q} V_{\text{int}} \quad (6.6a)$$

Upon substituting V_{int} from Eq. (6.5) one obtains

$$F = E \frac{\partial \mu}{\partial q} \quad (6.6b)$$

Combining Eq. (6.4) and (6.6b), the force is

$$F = 2Eqe^* \quad (6.7)$$

The latter force is then the driving force which can be used in the classical description of a forced harmonic oscillator through the differential equation

$$\ddot{q} + 2\eta\dot{q} + \omega_0^2 q = \frac{2e^*}{M_R} Eq \quad (6.8)$$

where η is a damping constant, ω_0 is the resonant frequency of the dipole oscillator and M_R is the reduced mass. From Eq. (6.8), one sees that the amplitude of the forced oscillator is proportional to e^* , and the energy to $(e^*)^2$. This is the physical origin of the quadratic dependence on e^* in Eq. (3.14) in Chapter 3.

The expression for the dipole moment in Eq. (6.4) is very limited, since it only describes a permanent dipole moment. A more general expression can be written as

$$\mu = \mu_s + \frac{\partial \mu}{\partial q} q \quad (6.9)$$

where μ_s is the "static" dipole moment and $\frac{\partial \mu}{\partial q} q$ is dynamic dipole moment. Since μ_s is not associated with a molecule's vibration, it is not of interest here. The term $\frac{\partial \mu}{\partial q}$ has

the units of charge and is called the effective charge, which would be e^* if the dipole were described by Eq. (6.4). However, the dynamic dipole does not have to be zero when the static charge transfer is zero. Such a dynamic dipole arises from the flow of charge between the two atoms when they vibrate against each other. An example that illustrates this phenomenon is the surface phonon observed on the (2×1) reconstruction of the (111) silicon surface.³³

In the case of H adsorption on a semiconductor surface, the dynamic charge flow between H and the substrate atoms is not known. It is therefore difficult to determine precisely to what extent the dynamic charge flow contributes to the amplitude of a measured loss feature. A rough estimate, however, can be obtained by comparing the measured effective charges (see Table 2) to those derived from the permanent dipole moments of AsH_3 and PH_3 (Ref. 67). Experimental dipole moments for AsH_3 and PH_3 are measured by a microwave method.⁶⁷ The values are $0.11 \text{ e}\text{\AA}$ for PH_3 and $0.042 \text{ e}\text{\AA}$ for AsH_3 . Assuming the angle between each bond pair is 99° (Ref. 68), one obtains for the dipole moment of the P-H bond $0.076 \text{ e}\text{\AA}$, and for that of the As-H bond $0.029 \text{ e}\text{\AA}$. Taking $1.5 \text{ \AA}$ as the separation between H and the As or the P ion, the static charge transfer is then derived as 0.051 e for P-H and 0.02 e for As-H. These values are only slightly smaller than the effective charge obtained from our measurement. Therefore, we conclude that the dynamic charge flow along the bond is not very important in the bond between H and the substrate atoms.

Questions may arise as to why the effective charge for the Ga-H bond in GaP is more than twice that of the same bond in GaAs when their vibrational frequencies are essentially the same. In fact the effective charge and the vibrational frequency are not closely related. The vibration frequency is primarily determined by the covalent character of the bond, which is the dominant bonding force in H-

substrate bond. The effective charge, on the other hand, is derived from the small difference in electronegativities and only serves as a measure of the interaction between the dipole and the probing electrons.

Chemisorption Induced Modification of The Cleaved Surface Relaxation

Let us first examine the effective charge for the cation-H stretch mode. The atomic orbitals involved in the bond formation are mainly the hydrogen 1s orbital and the cation dangling bond. The bond is highly covalent, and thus the charge density in the bond cannot be small. Since hydrogen is more electronegative than the cation it is expected that the H atom takes charge from the cation. Such a charge transfer may be described as a shift of the electron clouds in the covalent bond towards the H atom. On the reconstructed surface, which has an empty dangling bond, such a charge transfer cannot be realized. It is then necessary that charge redistribution among surface cations and anions occurs in order to accomplish a charge flow from the cation to the H atom. A simple redistribution is the back transfer of charge from the anion dangling bond to the cation dangling bond. As discussed earlier, reconstruction minimizes the total energy by lowering the electronic energy by more than the increase of elastic energy. Thus, when the electronic structure changes because of the back transfer of charge, the geometry of the relaxed surface is no longer favored. From the above discussion one sees that simply because charge is transferred from the cation to hydrogen, the relaxation must experience some healing. Theoretical calculations⁶⁹ reveal that the H chemisorption on Ga of GaAs lowers the total energy by 2.25 eV in comparison to the relaxed surface, and H chemisorption on As lowers the total energy by 3.03 eV. The total energy gained by relaxation is about 0.5 eV per surface atom, far less than the H chemisorption energy. Thus it is not surprising that

the relaxation is no longer very important. Direct evidence for H-induced healing of the surface relaxation for cleaved GaAs(110) and InP(110) is reported in the LEED study by Proix *et al.*;⁵¹ where dramatic changes in the LEED I-V curves are observed after the surface is exposed to atomic hydrogen. The resulting I-V curves are consistent with the bulk terminated surface. Indirect evidence found in the photoemission study of the H/GaAs system⁵² shows that the measured density of states agrees with the theoretical calculation by Manghi *et al.*⁷⁰ for H adsorbed on the unrelaxed dangling bonds.

Similarly, H chemisorption on the surface anion also suggests a redistribution of surface charge. Since P and As are more electronegative than H, charge is transferred from H to P and As as in the case of AsH₃ and PH₃. On the reconstructed surface, where the anion dangling bond is almost filled, the charge transfer from H to the anion is impossible. The charge redistribution must occur between the anion dangling bond and cation dangling bond, and this redistribution tends to heal the cleaved surface relaxation. As mentioned earlier, the formation of the As-H bond indeed lowers the total energy, by 3.03 eV compared to the relaxed geometry.⁶⁹ Thus, observation of an anion-H bond also indicates that the surface relaxation is removed.

The Role of Ionicity

Let us examine the charge transfer in more detail. We first discuss the Ga-H bonds for GaAs and GaP. The differences in the effective charges must be attributed to the presence of different nearest neighbors in the two crystals. Since P is more electronegative than As, one expects that more charge will be transferred from H to P than to As. In fact, the static dipole moment of PH₃ (0.11 eÅ) is larger than that of AsH₃ (0.042 eÅ). One could thus argue that in the H/GaP(110) system,

because of a larger charge transfer from H to P in the P-H bond, the neighboring Ga atom feels the increase of the negative charge and, consequently, the electron clouds in Ga-H bond will be pushed toward H. The net result is an increase of effective charge in both bonds. A similar argument can be applied to GaP and InP, where the cations are different. Hydrogen takes more charge from In than from Ga. Thus for InP, a more positively charged neighboring atom attracts the electrons in the P-H bond towards P. The argument can be made more general. The ability of the anion to attract electrons from H and the ability of H to attract electrons from the cation can be related to the ionicity of the crystal. In fact the Phillips ionicity⁴⁴ increases in the sequence GaAs, GaP and InP. The measured effective charges of both the cation-H and the anion-H also increase in the same sequence. Table 4 lists the effective charges and Phillips ionicities for the crystals.

This analysis has demonstrated that the intensities for the adsorbate-substrate vibrational modes on semiconductor surfaces contain much information about the chemical and electronic properties. More experimental and theoretical studies need to be performed to extend the application of HREELS to the investigation of semiconductor surfaces.

Table 4 List of the effective charge of H-substrate bonds and Phillips ionicity of the samples

	GaAs	GaP	InP
Phillips ionicity	0.310	0.374	0.421
Effective Charge			
Cation-H	0.036e	0.086e	0.11e
Anion-H	0.025e	0.060e	0.072e

Vibrational Frequency

The vibrational frequencies for the hydrogen-substrate atom bond also reflect the chemical properties of the bond. In a simple harmonic oscillator picture the frequency is directly related to the force constant k by $\omega^2 = k/M_H$, where M_H is the mass of the hydrogen atom. From the data, the measured frequencies are in the following sequence: $\text{In-H} < \text{Ga-H} \approx \text{Sb-H} < \text{As-H} < \text{P-H}$. Thus, the force constants are in the same order. For small molecules, it is known that the force constants are a function of the equilibrium distance and the dissociation energy.⁷¹ By definition the force constant is the second derivative of the interaction potential, not the depth of the potential well (the dissociation energy). Nonetheless, it is almost always true that the stiffer the bond, the higher the dissociation energy.⁷² The equilibrium distance is, however, easier to relate to the force constant. The closer together the two atoms are, the narrower the potential well is, and thus the larger its second derivative (force constant) is. In the hydride system X-H (X denotes any element), the trend is as follows. Along any one row of the Periodic Table, the electronegativity increases as the nuclear charge increases. Thus in the X-H bond, the electron of the hydrogen atom is attracted more toward the X atom. The lighter hydrogen atom moves towards the X atom to maintain maximum electronic overlap. The frequency then increases because the bond length shortens and the dissociation energy increases. As one passes down one row, the dominant factor is probably the radius change (bond length increase). These arguments can easily explain the observed sequence of frequencies in the experiments noted earlier. However, the frequencies of the cation- H stretches are considerably larger than for the cation- H diatomic molecules, whereas the frequencies of the anion- H stretches

are very close to those of the corresponding hydrides. The similarity of the anion-H bonds with those of the hydrides can be explained by noting that in both cases the anion has a similar number of nearest neighbors: the surface anion has four neighbors (including the adsorbed H atom) and the anion in the hydrides has three neighbors. For the cation-H stretch, the configuration changes dramatically from adsorption complex to hydride, in that the surface cation has four neighbors whereas the cation in the molecules has only one.

The Effects of Sputtering

Our experimental results demonstrate that a dramatic change in the surface properties occurs when the surface is lightly sputtered. In the data, it is a general trend that for the sputtered surface the ratio of anion-H stretch intensity to that of the cation-H stretch is enhanced over the ratio for the cleaved surface. In particular, for InP, the ratio is enhanced by a factor of 40. Three possibilities are discussed here. a) The cation sites are passivated by the sputtering; b) the cation-H bonds are not dipole active or not favored by the selection rule, in which only the dipole moment perpendicular to the surface can be detected; c) there is an increase of the effective charge in anion-H bonds and/or a decrease of the effective charge in cation-H bonds. Here the stoichiometry change on the surface is not considered since the XPS data reveals that such an effect is minimal.

The intensity of the H-substrate vibration is quadratically dependent on the effective charge (see Eq. (3.13)). Thus the enhancement of the P-H stretch observed for InP corresponds to a six-fold increase in the effective charge for the P-H bond. Accordingly, the dipole moment of the P-H bond will significantly exceed that of the P-H band in PH_3 . Although the back bonds of the surface P could be different

after sputtering from those of the cleaved surface, where the bonding partner is In, such a huge dipole moment seems unphysical. Therefore the change in the dynamical charge in the H-substrate bonds is not significant for InP. For GaP, the enhancement is about a factor of two, and for GaAs, the enhancement is even smaller. For these two samples, the change of the effective charge may possibly account for the intensity change.

It is also possible that some cation-H bonds may lie parallel to the surface, in which case the dipole interaction would be weak. Physically, it is difficult to imagine that all the cation-H bonds would be parallel to the surface.

Schaefer *et al.*⁶⁰ first proposed the idea of surface cation passivation after sputtering, but no detailed model was suggested to interpret the passivation. In our data, one sees that the strong passivation of surface cations occurs on InP, InAs and probably InSb. As in the case of InP, H adsorbs to As on the sputtered InAs surface at room temperature, while the In-H mode is very weak or not present. In the case of InSb, the In-H mode is also depressed although quantitative conclusions are excluded because of the overlap of water's scissor mode. It is believed that the largest passivation effect for the surface cations occurs on samples which contain In.

The effects of sputtering are complicated. It may produce an amorphous layer⁷³ and preferential sputtering may also occur.^{74,75} In our experiments, the ion energy and total ion dose are small enough so that preferential yields are not significant.⁷⁵ In addition, our XPS data have revealed that the surface stoichiometry change is much too small to account for the changes in anion-H to cation-H intensity ratios. However, XPS is not a microscopic probe, and local In clustering and anion segregation cannot be excluded. If microscopic patches of In and the anion are formed during the sputtering, the In cluster would behave more like a

metal and may be inactive for H adsorption. Although clustering of cations^{44,76} and the segregation of anions⁷⁷ have been reported on a larger scale, the observations of the metal island formation have not been extended down to the microscopic scale, e.g. below 1000 Å, because of limitations in instrumental spatial resolution. Nonetheless, it may well exist. On such a surface, the metal cluster would be inactive to H adsorption, whereas the anion and H could form compounds such as PH₂, PH₃, etc. In fact, for heavily hydrogenated GaAs(110) and InP(110) surfaces, the adsorbed AsH₃ and PH₃ are responsible for the photoemission "black hole" in the photoemission yield study of Proix *et al.*⁷⁸

Sputtering also dramatically changes the adsorption kinetics in that after sputtering the chemisorption occurs at higher temperatures than on the cleaved surfaces. Although the implication could be complicated, it may stimulate more investigation.

In conclusion, it is believed that the passivation of the cation after sputtering is due to the strong local In clustering on the surface of the In-containing III-V compound. Such a sputter-induced clustering is independent of the crystal orientation, and as a consequence the passivation effect should be observed on other surfaces. In general the effect may exist for other molecules adsorbed on these surfaces. For Ga-containing compounds, the clustering probably is not very strong, and the basic surface atomic structure is a tetrahedrally-bonded amorphous-like layer, with chemical properties that are closer to those of cleaved surfaces.

CHAPTER 7

CONCLUSIONS

In this thesis, two aspects of the III-V compound semiconductor cleavage surfaces were studied.

First, the dynamic response of the conduction band free carriers and their coupling with the optical phonon in the space charge region were investigated.

As an example exhibiting a depletion-type space charge layer, the GaAs(110) cleaved surface was studied. The doping level was chosen to be quite high so as to resolve the plasmon peak in the HREELS spectrum. For the first sample, the plasmon was clearly resolved at near 75 meV, with the exact position depending on the surface condition. This peak is more prominent at high primary-electron energy because of the larger probing depth for high-energy electrons. The coupling of the plasmon with the optical phonon for this sample is revealed by the damping of the phonon intensity caused by these free electrons. The energy positions of the plasmon and phonon are not much affected by the coupling because their eigenmode frequencies are far apart. On clean cleaved surfaces, the bands are almost flat up to the surface, if quantum mechanical effects are neglected, and the plasmon loss is found at near 81 meV. As time elapses, or with deliberate hydrogen exposure, the plasmon peak shifts down in energy and decreases in intensity, while the intensity of the phonon peak increases. This effect is attributed to space charge layer formation. In this layer the free electrons are repelled from the surface region into

the bulk by surface state electrons, and consequently the plasmon mode moves towards the interface between the space charge layer and the bulk. Such a movement results in a downward shift in energy of the plasmon loss feature, and a reduction in its intensity. Moreover, the phonon peak in the depletion layer is enhanced in intensity because of the absence of electrons. A simple two-layer model was used to correlate the plasmon energy position with the space charge layer parameters. The band bending inferred by calculation is in rather good agreement with published data. The method used in this investigation is especially sensitive at the initial stage of the band bending, a stage which is difficult to characterize with other techniques.

On the second sample, the coupling of the plasmon and the phonon was very strong because their energies are nearly equal. The shift of the phonon was also observed. The strong coupling and high instrumental resolution make it possible to observe three losses: two features associated with the coupled plasmon and phonon below the depletion layer, and one associated with the bare phonon in the depletion layer. Due to the closeness of these peaks, the line shape rather than the peak position is strongly affected by the surface conditions. As the depletion layer forms, the intensities of the two coupled modes decrease while that of the bare phonon increases. A two-layer model was employed to calculate the line shape of the loss structures and the band bending parameters. The line shape fitting gives good agreement with published value of the band bending. The data for the clean surface also reveals the existence of an intrinsic electron depleted region, which comes about because of the so-called quantum mechanical effect. The existence of this depleted region was inferred from the presence in the spectrum of a bare-phonon peak, and a calculation showed the thickness of the region to be approximately 100 Å.

The InAs(110) cleaved surface was studied because it is an example of a surface with an accumulation layer. On this surface, a fairly strong accumulation layer is formed when the surface is exposed to atomic hydrogen. The electrons are highly concentrated at the near-surface region and thus many characteristic properties are different from those of the depletion layer. The plasmon energy increases as the space charge layer is formed simply because the electron density increases. As the plasmon energy approaches the phonon energy, the plasmon-phonon coupling becomes stronger and new modes are formed, each a mixture of the two original modes. The characteristic width of the plasmon loss line is substantially larger than the FWHM of the elastic peak; the difference is attributed to the highly nonuniform electron density in the accumulation layer. In contrast to the case of the depletion layer, the bare phonon in the bulk below the accumulation layer is not observed because it is screened by the high density of electrons in the near-surface region. However, the bare phonon in the intrinsic electron-depleted region is observable at low primary energy, where the probing depth of the incoming electron is small.

The experimental and theoretical methods used in this investigation are generally applicable to other semiconductor surfaces and interfaces. Among various possible applications, one would expect the study of the following systems to be profitable. First, thin-film semiconductor interfaces or layered structures grown by molecular beam epitaxy or other methods represent one class of materials which are ideal for HREELS investigation. Studies of the electron dynamical response of these systems could provide information valuable for the understanding of the fundamental physical processes that occur in these devices and for the design of quantum well structures and superlattice devices. Second, the extreme sensitivity of HREELS spectra at the initial stage of band bending may provide clues for the understanding

of the initial stage of Schottky barrier formation, which has been a subject of study for many years. Finally, the study of plasmon excitations at low temperatures could be useful. When the impurity concentration is high enough so that a band is formed, the plasmon structure will allow one to study the behavior of electrons in these states. In an accumulation layer, low temperatures could result in occupation by electrons of only one sub-band, and thus the plasmon would be truly two-dimensional. Needless to say the two-dimension electron gas is a very interesting system.

The second subject of the thesis is the chemisorption of hydrogen on III-V (110) cleavage surfaces. It was found that H adsorbs on both the surface cation and anion via their dangling bonds. Preferential adsorption was not observed throughout the exposure range. For GaAs, GaP and InP, the adsorption occurs at room temperature, whereas for GaSb, InSb and InAs, adsorption was only observed at lower temperatures (below 120 K). Surface damage due to H-substrate interaction was also apparent in the reduction of the elastic peak intensity and the higher background in the LEED pattern.

The effective charges transferred in H-substrate bonds were calculated for GaAs, GaP, and InP and were found to increase in the sequence GaAs, GaP, and InP. An argument based on the electronegativities of these elements was employed to interpret the results. The model also led to the conclusion that the surface relaxation is healed.

The frequencies of H-substrate stretch modes were interpreted in terms of the electronegativity of the elements as well as the H-substrate bond lengths. The frequencies were also compared to the corresponding hydrides and diatomic molecules, and the discrepancies were interpreted based on the difference of the nearest neighbors between crystal and hydrides or diatomic molecules.

H chemisorption on lightly sputtered surfaces was also investigated. It was generally observed that the anion-H stretch intensity is enhanced relative to the cation-H stretch intensity in comparison to the case of the unperturbed cleavage surface. The enhancement was particularly strong for samples containing In. We proposed that the local In clustering due to sputtering is responsible for the passivation of surface In atoms.

In summary, we have investigated the electronic and chemical properties of the cleavage surfaces of III-V compound semiconductors. The results obtained are valuable for studies in the field of semiconductor surfaces.

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