Electric Field Induced Raman Scattering at the Sb–InP(110) Interface: The Surface Dipole Contribution

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Using the prototypical interface of Sb on InP(110), it has been shown that strong local electric dipole fields may arise at semiconductor surfaces which need to be considered in addition to band bending-induced electric fields for explaining electro-optic effects. Symmetry forbidden LO phonon Raman scattering, which has been often used in the past to analyze internal electric fields related to band bending, is a suitable optical probe. The surface local dipole field, related to reconstruction or relaxation-dependent atomic displacements in the outermost atomic planes, delivers a significant contribution to the forbidden LO phonon scattering, in addition to the band bending-related Schottky field. Taking this into account, apparent inconsistencies of the electric field-induced Raman scattering (EFIRS) and photoemission spectroscopy from the previous work can be resolved.

1. Introduction

Electric fields at semiconductor surfaces and interfaces are a very common and important issue. Surface electric fields due to the Fermi level pinning extend usually some 10–100 nm in depth, dependent on the surface band bending and bulk doping concentration. In addition, a strong local electric field may arise at surfaces and interfaces of compound semiconductors, related to the atomic displacements of the partially charged atoms in the respective crystal sublattices.[1–3] Both fields have considerable impact on device properties of semiconductors-like rectification in Schottky contacts, work function at semiconductor surfaces, band offsets at heterostructure interfaces as well as wavelength and intensity of light emission or absorption.[2–4] The polarization field at surfaces and interfaces depends on the partial charge of different atomic species in the compound, on the crystal lattice, and on the displacement of the atoms from their regular lattice sites and accompanied charge redistribution due to strain or surface reconstruction.

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If one considers the prominent class of zinc blende compound semiconductors (III–V, II–VI), the electric field in the bulk crystal vanishes due to symmetry (in contrast to wurtzite structures of the respective compounds). However, this is no longer valid if the crystal surface is considered. A considerable part of the electronic work function of such compound semiconductors is related to the atomic structure of the surface, i.e., uppermost atomic layers.[5] Assuming a truncated bulk crystal, the dipole field would be simply related to the relative occupation of the two elements in the surface plane, i.e., the more electronegative group V or group VI and the less electronegative group III or group II species of the compound crystal. However, on real surfaces the reconstruction has to be taken into account since it induces atomic displacements of atoms from their bulk-lattice sites in the uppermost atomic layers. Moreover, the chemical bonding configuration of the surface atoms differs from that of the bulk crystal, thus additional electronic charge transfer arises between the anion and cations in the surface layers. Similarly, at heterostructure interfaces such dipole fields exist, e.g., from atomic displacement related to the epitaxial strain.[2,5] In fact, whether surfaces, heterointerfaces, or nanostructures are considered, microscopic strain occurs on the length scale of some lattice constants, leading to associated strong local electric fields.

In comparison to the doping-related Schottky-field, the surface local field induced by the charge transfer and atomic displacements extends on a considerably smaller length scale of only few atomic layers. On the other hand, such local fields in polar compound semiconductors may become several orders of magnitude larger than the Schottky field and thus influence significantly opto-electronic properties of semiconductor nanostructures.[2,6,7] Lastras-Martinez et al.,[7] for instance, have shown on GaAs(001) that the surface reconstruction induces a strain-related local field which contributes significantly to the linear electro-optic effect (LEO) at the $E_1/E_1+\Delta_1$ gap.

In the present work, we will demonstrate that such a link exists also between the surface dipole field and the electric field-induced Raman scattering (EFIRS). EFIRS means the symmetry forbidden LO-phonon Raman scattering in zinc blende materials which is induced by a symmetry reducing external electric field. This scattering mechanism was worked out some decades ago and is used to determine Schottky barriers at metal–semiconductor interfaces.[8–10] The EFIRS work was

motivated by the controversy on the understanding of the Schottky barrier formation, i.e., for establishing EFIRS as a monitor of the surface electric field in the space charge region. It was demonstrated, for instance, by placing semiconductors in an external electric field that the EFIRS LO-phonon scattering amplitude is indeed related linearly to the electric field strength, and thus the LO scattering intensity proportional to the square of the electric field.[10] Consequently, the LO EFIRS intensity should be a measure of the surface band bending potential in the space charge region. Several applications on III-V-semiconductor surfaces and metal-III-V-semiconductor contacts were published.[11,12] However, a quantitative agreement of Schottky barriers determined from EFIRS and photoemission spectroscopy was often not achieved, such as in the case of Sb on *n*-doped InP(110).[13–15] In the following we will show that the neglection of the surface dipole field which appears at the relaxed semiconductor surface due to the differently charged anions and cations is responsible for the discrepancy. Here we will concentrate on the unrelaxation of the InP(110) surface induced by Sb adsorption which gives rise to changes in the surface dipole field.

2. InP(110) Surface and Sb Monolayer Structure

The effect of surface local fields can be demonstrated by looking at the Sb/InP(110) interface. On the one hand, it is very well understood with respect to its atomic structure and, on the other hand, has been intensively characterized by both EFIRS and photoemission spectroscopy.[13–15] Sb on InP(110) forms an atomically sharp and very well-ordered interface. The adsorbed Sb atoms are known to epitaxially continue the structure of the bulk material (epitaxially continued layer structure, ECLS), i.e., the first monolayer of Sb on InP(110) adopts nearly the positions of the hypothetical next InP layer (see **Figure 1**). The atomic and electronic structure of the clean as well as the Sb monolayer-covered InP(110) is very well known, since many experimental investigations including scanning tunneling microscopy/spectroscopy (STM/STS), photo electron spectroscopy (XPS/UPS), Raman spectroscopy, low energy electron diffraction (LEED), and theoretical calculations[5] have addressed this model system leading to a fully consistent picture. In the coverage regime between 0 and 1 monolayer (ML) of Sb, the adatoms allocate in patches of the monolayers structure leaving uncovered InP regions exposed in between. When 1 ML of Sb coverage is reached, the ideal monolayer structure has been built up on the InP(110) substrate surface. We note that the clean InP(110) surface has a relaxed surface geometry, i.e., the negatively charged P atoms move outward the surface while the positively charged In atoms inward. The electronic configuration of these two atoms differs from the bulk situation: the outer P atom has three *p* bonding orbitals and one doubly occupied nonbonding *s* orbital (in total five electrons), while the In atom has only three electrons in three bonding sp_2 orbitals. Accordingly, a large surface dipole arises due to the relaxation within the first atomic layer of the (110) plane which, to the contrary, is neutrally charged in the bulk.

Ab initio calculations, photoemission spectroscopy, and STS show that the clean InP(110) surface is free of surface electronic states.[5] At the Sb monolayer-terminated surface, electronic states are found quite close in energy to the conduction band edge. Accordingly, the Fermi level shift (referring to the surface band bending) is expected to be zero at the clean surface and small or very small at the Sb monolayer-terminated one for *n*-doped InP(110) substrate. Exactly this behavior is found in SXPS experiments published by Zahn et al.[15] in 1989 on n-type InP(110) (see **Figure 2**). At the clean surface flatband condition occurs, i.e., the surface Fermi level position is equal to the bulk Fermi level. Upon Sb deposition a band bending evolves inducing a surface Fermi level shift and subsequently, for coverages approaching 1 ML, the band bending decreases again. This behavior is expected: for sub-monolayer coverages, at room temperature regions of the Sb monolayer are formed in coexistence with still uncovered regions. At the border of the Sb monolayer regions surface states are generated which induce the Fermi level shift (band bending). With higher Sb coverages the density of surface states is lowered, since an increasing part of the surface is covered with Sb. Consequently the Fermi level shift is reduced.[5,14,15] For deposition at 100 K, to the contrary, the Sb overlayer is disordered and the ECLS monolayer structure is not formed. In this case, the Fermi level shift (band bending) increases with Sb deposition and saturates around monolayer coverage.

3. EFIRS Results

The EFIRS data discussed in the following were originally published by Esser et al.[14] in 1987. They show a completely different behavior than the data derived from photoemission

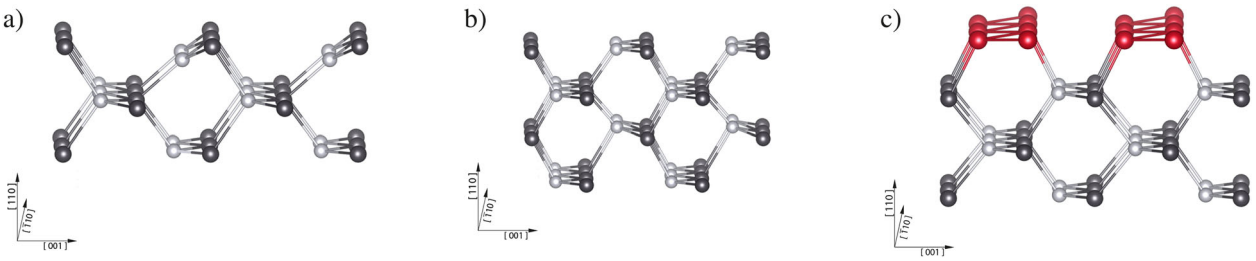

Figure 1. Perspective side view showing the atomic geometry of the InP(110) surface. a) Relaxed surface structure with P and In atoms of the uppermost (110) plane displaced outwards and inwards, respectively. This refers to the minium energy configuration of the clean surface. b) Ideal, unrelaxed (110) surface. In and P atoms of all (110) planes reside in the bulk positions. c) Sb monolayer terminated surface. In and P atoms of the first (110) plane are nearly in the bulk-like position.

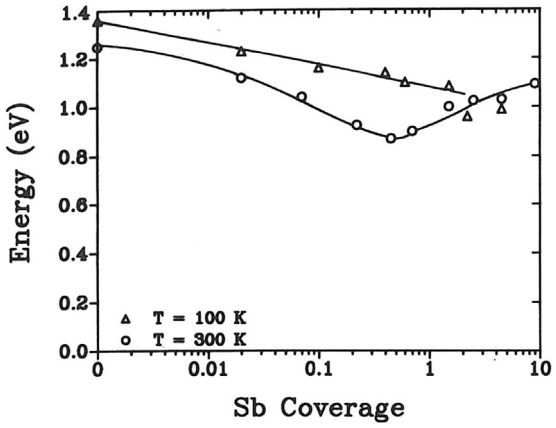

Figure 2. Dependence of the surface Fermi level position on *n*-doped InP(110) on Sb coverage for 300 and 80 K sample temperature. On the clean-cleaved surface flatband conditions are present, since no acceptor-type electronic states exist in the bandgap on the relaxed InP(110) surface. The Fermi level positions at the clean surface are equal to the respective bulk Fermi levels. Adsorption of Sb atoms induces surface states and a band bending evolves. At 300 K the Sb allocates in the ordered ECLS monolayer structure. At 100 K adsorption, to the contrary, the regular monolayer structure is not formed and disorder-related surface states remain present. Reproduced with permission.[15] Copyright 1989, Elsevier.

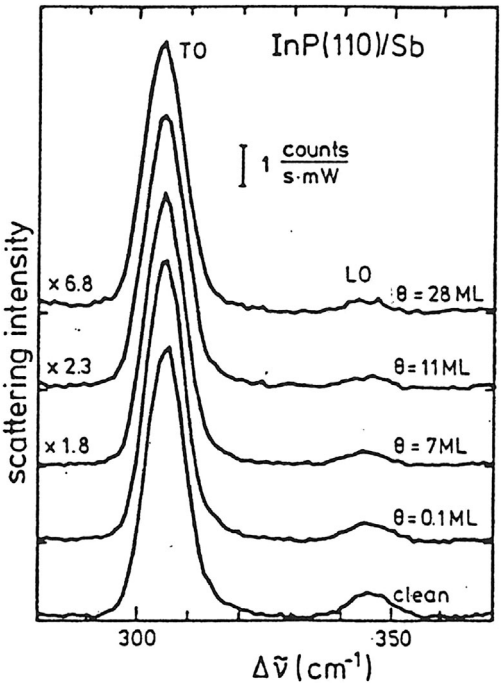

Figure 3. Raman spectra on InP(110) in the TO and LO phonon spectral range as a function of Sb coverage. The TO phonon is symmetry allowed, the LO phonon symmetry forbidden. Reproduced with permission.[14] Copyright 1987, AIP Publishing.

spectroscopy. The evolution of the TO and LO phonon spectra of InP(110) with increasing Sb coverage is shown in **Figure 3**. The Raman spectra of InP(110) were taken at 406.7 nm (3.048 eV) Kr-laser excitation which is near to the E_1-gap of InP (3.16 eV at 295 K) (the resonant excitation to the E_1 band gap is mandatory for the observation of the symmetry forbidden LO phonon scattering).

Maximum LO phonon scattering intensity arises at the clean surface, while with Sb deposition up to a few ML the EFIRS intensity decreases strongly.[13,14] If one evaluates the band bending from the LO phonon scattering based on the surface electric field, one expects the following relationship of the LO/TO ratio to the surface band bending potential[11,12,14]

$$\frac{I(\mathrm{LO})}{I(\mathrm{TO})} = C \int_0^d \left[E^2(z) \cdot \exp(-2az)\right] dz \qquad (1)$$

where $E(z)$ stands for the electric field and d is the penetration depth of the light (27 nm at 3.05 eV), see **Figure 4**.

Figure 5 shows the according development of the so-called "band bending" as determined from the LO/TO ratio. The "band bending" at the clean surface of around 0.3 eV decreases with Sb coverage to approximately zero after forming a full monolayer. For further deposition of Sb at room temperature (RT), a re-increase of the "band bending" is observed for higher Sb coverages associated with a structural phase transition from amorphous to crystalline Sb[16] (this transition is not observed for 90 K sample temperature). For the purpose of the present paper, it is essential to note that the "band bending" is nonzero at the clean surface and diminishes to zero around ML coverage. Obviously, the observed EFIRS intensity is not related to the Schottky field at all. As we will argue, the EFIRS intensity, to the contrast, is dominated by the evolution of the surface dipole field.

This is immediately evident by looking at the structure changes of the InP(110) surface upon Sb deposition: the clean InP(110) surface is relaxed. In the first atomic layer, the electronegative P atom is significantly moved outwards and the electropositive In atom significantly inwards.[13] As a consequence, a strong surface dipole field arises yielding an increase in work function (we will come back to the surface dipole potential in the next section in detail). Upon deposition of Sb, the relaxation of the InP surface layer is quenched, and, accordingly, the surface dipole field significantly reduced.[13] Thus, the decrease in LO EFIRS intensity upon Sb deposition just reflects the reduction of the surface dipole field associated with increasing surface part covered with a Sb monolayer. As mentioned above, the re-increase of the LO EFIRS intensity for several ML Sb is related to the crystallization of the Sb overlayer on top of the Sb-monolayer-terminated InP substrate.[14,16] Thus, crystallization of the Sb induces a surface strain which is reflected by an increasing dipole field and accordingly increasing LO EFIRS intensity. As we would like to note the crystallization of Sb can be suppressed by deposition at liquid nitrogen temperature, and in that case no re-increase of the LO/TO ratio occurs.

The decrease of the "band bending" from LO/TO occurs in both RT and low temperature (LT) cases. This means that the relaxation of the InP surface is quenched in both cases by the Sb deposition, due to the chemical interaction of the adsorbate with the substrate. In both RT and LT cases, the EFIRS intensity thus depends on the relaxation/unrelaxation effect. Only in the RT case the regular ECLS monolayer structure is formed, while at LT deposition the Sb overlayer is disordered. Accordingly, only for

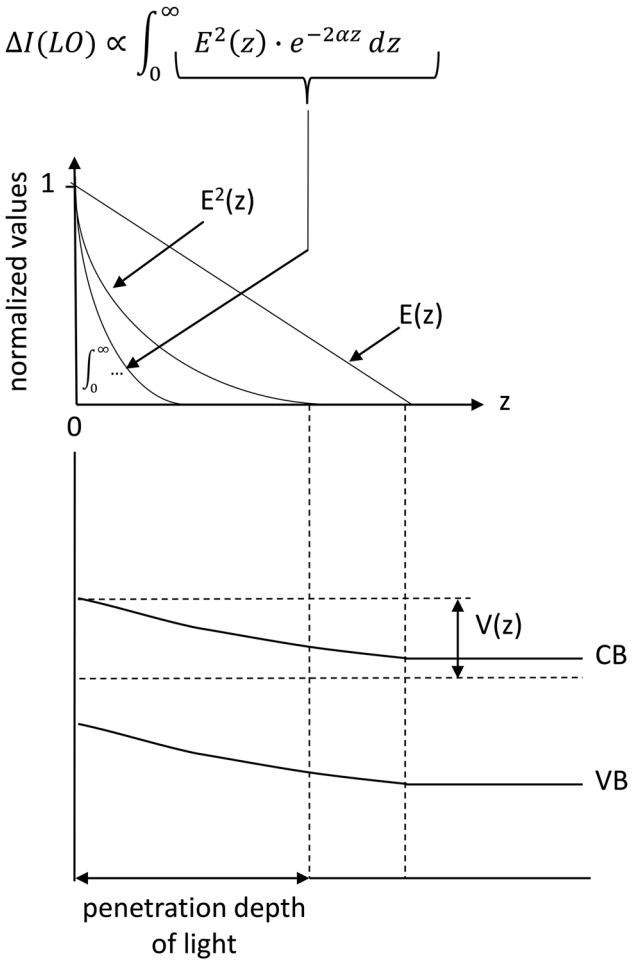

Figure 4. Relation between electric field and penetration depth of light in the space charge region of low *n*-doped InP. Only the linear Schottky field is shown. V_{SB} denotes the Schottky barrier. The surface dipole field is not included here.

RT deposition the band bending vanishes at ML coverage while at LT the increase of band bending saturates around monolayer coverage.

Thus, summarizing the Schottky barrier behavior, the photoemission results at RT as well as LT show flatband after cleavage in UHV followed by an increase in band bending upon Sb deposition in the submonolayer coverage regime. The LO EFIRS intensity, to the contrast, shows no correlation to the band bending. Instead the LO/TO ratio is apparently correlated with the unrelaxation of the InP(110) surface induced by the Sb deposition at submonolayer coverages.

4. Electron Potential

In order to illustrate and substantiate the above conclusion, we used density-functional theory in the local-density approximation (DFT-LDA) to calculate the electron potential at the surface of the clean ideal as well as structurally relaxed InP(110) surfaces and at the monolayer Sb-covered InP(110) surface. The Vienna

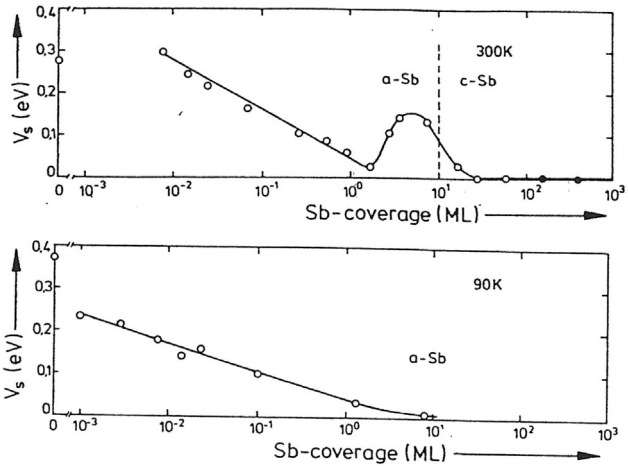

Figure 5. Band bending as a function of Sb coverage at 300 K (a) and at 90 K (b). Open circles refer to EFIRS data, filled circles to *I–V* measurements. a-Sb, c-Sb: amorphous, crystalline Sb. Reproduced with permission.[14] Copyright 1987, AIP Publishing.

ab initio simulation package[17] implementation of DFT is used to determine the surface structural and electronic surface properties. The surfaces are modeled within periodic supercells, consisting of 24 atomic layers stacked along the surface normal. An additional layer contains the Sb surface atoms. A vacuum region of 25 Å decouples the slab from its periodic images along the surface normal. The Brillouin zone is sampled using a $4 \times 4 \times 1$ k-point mesh. The atomic geometry and the electronic structure are simultaneously relaxed to determine the surface ground state.[5] The calculated atomic geometries of clean ideal, the structurally relaxed InP(110) surface and the monolayer Sb-covered InP(110) surfaces are shown in Figure 1. They correspond closely to the atomic structures known from experiment and earlier calculations, see, e.g., refs. [5,18]. The surface dipole and the accompanying electrostatic potentials which cause the changes of the work function upon structural relaxation and/or group-V adsorption can be obtained from the microscopic electron potential calculated within DFT-LDA. Since we are especially interested in the macroscopic spatial dependence of the potential in [110] direction, it is convenient to perform a planar ((110) plane) average of the potential according to

$$\bar{V}(z) = \frac{1}{A}\int_A dx dy V(x, y, z) \tag{2}$$

where A corresponds to the area of the surface unit cell in the (110) plane. **Figure 6** shows the planar averaged potential along the surface normal.

The plot shows distinct differences between the potential calculated for the clean-relaxed InP(110) surface compared to the unrelaxed, i.e., structurally ideally bulk-truncated InP(110) surface. These differences are particularly obvious in the uppermost two atomic layers and result from the above-mentioned charge redistribution associated with the relaxation, which causes a strong electric dipole field within the first two layers. The dipole associated with the charge redistribution

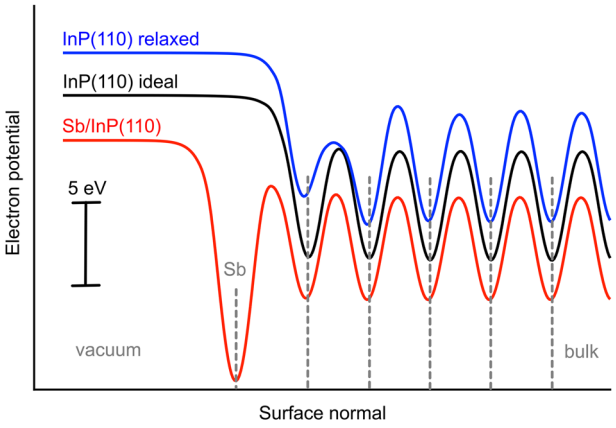

Figure 6. Planar averaged (see text) electron potential calculated (DFT-LDA) for clean relaxed, clean unrelaxed (ideal), and monolayer Sb-terminated InP(110) surface plotted along the surface normal. The positions of the InP and Sb atomic planes are indicated by dashed lines.

increases the calculated work function of the InP(110) surface by 0.29 eV. Upon Sb termination, the structural relaxation of the InP(110) surface is essentially lifted as shown in Figure 1. Also the electron potential of the first and second InP layer underneath the Sb overlayer is quite close to that of the hypothetical unrelaxed surface. According to our calculations, the Sb overlayer-related surface dipole reduces the work function of the InP(110) surface by 0.44 eV in comparison to the unrelaxed surface, i.e., the Sb termination has an effect opposite to the structural relaxation. We mention that there are electric fields also in the surface plane, e.g., related to the two inequivalent chemical bonding sites of the Sb in the monolayer structure which leads to a positively and a negatively charged Sb atom in each surface unit cell. This charging, yielding an in-plane electric dipole field, is evident in the core level shifts of according photoemission spectra.[19,20] However, it is not relevant for the EFIRS at the InP LO phonon mode since the latter originates from the electric field-induced modification of In-P bonds below the Sb monolayer.

We would like to note that both Schottky and dipole-related surface electric fields induce EFIRS scattering of the LO phonon. The electric field related to the Schottky barrier can easily be estimated from the band bending and the bulk doping concentration of the InP substrate. For a doping concentration of $6.10^{16}\,cm^{-3}$ as used in the referenced EFIRS experiments, the maximum band bending (0.3–0.4 eV, see Figure 5) corresponds to a surface electric field of $1.3 \cdot 10^5\,V\,cm^{-1}$ and a depletion layer width of 70 nm. The Schottky field obeys a linear decay across the space charge layer, from $1.3 \cdot 10^5\,V\,cm^{-1}$ at the surface to 0 at depth 70 nm. Due to the finite penetration depth of the light of 27 nm, the near surface region of the Schottky field is mainly sampled. The surface dipole field, on the other hand, is much stronger. According to our DFT calculations, a surface dipole contribution of the relaxed surface (as compared to the unrelaxed clean one) amounts to 0.27 eV. Since the surface dipole is related to the charge redistribution of the outermost (110) plane the associated electric field extends approximately on a thickness of 0.2 nm (single (110)-plane)). The electric dipole field then amounts to $1.5 \cdot 10^7\,V\,cm^{-1}$, i.e., two orders of magnitude above the Schottky field. According to this estimate the surface dipole field should be the dominant factor at low doping, while the Schottky field the dominant one for high doping, assuming a sufficient amount of band bending. We would like to note that this has indeed been observed.[19,20] On Sb/InP(110) with low n-doping concentration, however, the surface dipole field yields the by far dominating contribution.

Finally we would like to mention that a quantitative determination of the Schottky barrier by EFIRS suffers also from the surface photovoltage effect since Raman spectroscopy goes along with an intense above band gap laser illumination.[21] The surface dipole contribution, however, is independent of laser illumination since the dipole field can not be sceened by photoexited carriers.

5. Summary and Conclusions

In summary, we have re-addressed EFIRS data in the light of considering both Schottky as well as surface dipole fields. We show that surface dipole fields deliver a significant contribution to the LO EFIRS scattering intensity, a fact which has not been taken into account so far. EFIRS depends on electric fields related to surface or interface strain such as on reconstructed or relaxed surfaces, in addition to the Schottky field. In particular for low doping concentration EFIRS is a measure of local strain rather than of band bending.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

DFT calculations, electric-field-induced Raman scattering, InP, semiconductor surfaces, surface dipole

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