Photoreflectance studies of surface state density of InAlAs

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The surface barrier height and surface Fermi level of InAlAs were investigated via photoreflectance spectra. Surface state density was then determined from the surface barrier height as a function of temperature, illumination power intensity, and intrinsic layer thickness. Results obtained from these three independent approaches all give the same conclusion, that the surface states are distributed over two separate regions within the energy band gap. Closely examining the photovoltage induced by various incident beam intensities revealed that the photovoltage effect is negligible when the illumination power intensity is below 1.0 μW/cm². © 2001 American Institute of Physics.

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I. INTRODUCTION

The surface Fermi level is generally pinned in the energy gap by a sufficiently large density of extrinsic surface states of both donor and acceptor character on the real surface of semiconductors. These extrinsic surface states are attributed to surface defects of a hitherto unspecific nature. Since large surface state density may lead to high losses, low gains, and a short lifetime in semiconductor devices and solar cells, the determination of surface state density and Fermi level pinning has received increasing attention. Because of its contactless and nondestructive nature, modulation spectroscopy of photoreflectance has become important in studying the surface barrier height, surface Fermi level pinning, and doping concentration during the last two decades. Previous work has demonstrated that soft x-ray photoemission spectroscopy (SXPS), used in most previous studies of the surface Fermi level, can be replaced by photoreflectance when investigating surface and interface Schottky barrier formations as well as surface Fermi level pinning.

The ternary III–V compound InAlAs has recently emerged as a highly promising material for optoelectronic integrated circuits, high-speed electronic devices, and microwave devices. The InAlAs/InGaAs heterostructure is a particularly effective material system due to its large conduction band discontinuity, which creates a large two-dimensional electron gas concentration. Additionally, the small effective mass of this system ensures high mobility for high speed device operations with record high frequencies up to 360 GHz. For device design and application, information relating to the surface Schottky barrier height, surface Fermi level pinning, and surface state density are crucially important. Although the energy gap $E_g$ and spin–orbital splitting energy $\Delta_0$ have been widely reported, very few detailed contactless optical studies have been performed to determine surface barrier height, Fermi level pinning and surface state distribution for InAlAs heterostructures. Previous photoreflectance studies have found the Fermi level to be firmly pinned at the midgap in GaAs and GaAlAs. However, our earlier work investigating the energy band gap, built-in electric field, and surface Fermi level position of a series of In$_{1-x}$Al$_x$As surface intrinsic-$n^+$ structures (SIN$^+$) with varying composition $x$ and/or differing undoped layer thickness at room temperature via photoreflectance showed that this was not the case. Above an aluminum concentration of 0.42–0.57, the surface Fermi level was found to not be pinned at midgap, as commonly believed, but, rather, varying from 0.50 to 0.81±0.01 eV below the conduction band edge. Based on the dependence of electric field and surface Fermi level on the thickness of the undoped layer, we concluded that the surface states are distributed over two separate regions within the energy gap and that the surface state densities are as low as $(3.51±0.05) \times 10^{11}$ cm$^{-2}$ for the distribution near the conduction band and $(4.61±0.05) \times 10^{11}$ cm$^{-2}$ for the distribution near the valence band.

In this study, we used photoreflectance (PR) to measure the photovoltage as a function of temperature and pump beam intensity. First, we measured the photovoltage, at various temperatures, induced by the pump beam and probe beam, both maintained at constant and low intensities. Second, the photovoltage was measured at room temperature and was induced by various pump beam intensities with the probe beam maintained at a very low constant intensity. By fitting the experimentally measured dependency of photovoltage on temperature and pump beam intensity, respectively, to the theoretically derived relations, both the surface Fermi level and surface state densities are obtained from the fitting parameters. The results obtained from the two different conditions described above agree well with each other, as well as with the results of previous studies. Along with our new findings, in this article we also briefly review our earlier study of the determination of surface state densities and surface state distributions through the dependency of the surface Fermi level on the top layer thickness of the InAlAs SIN$^+$ structure.

II. THEORY

In PR, the surface electric field is modulated through the photoinjection of an electron-hole pair via a chopped incident
laser beam. The line shape of the PR signal, $\Delta R/R$, is directly related to the perturbed complex dielectric function. For a moderate electric field, the PR spectrum exhibits a series of oscillations [Franz–Keldysh oscillations (FKOs)] originating from the electric field $F$ in the samples.\textsuperscript{9,27} The $n$th extrema $E_n$ of FKO occurs when\textsuperscript{28,29}

$$n \pi = \left( \frac{3}{2} \right) \left[ (E_n - E_g)/\hbar \omega \right]^{3/2} + \chi,$$  \hspace{1cm} (1)

where $E_g$ denotes the energy gap, $\chi$ represents an arbitrary factor, and $\hbar \omega = (\varepsilon^2 \hbar^2 F^2/\mu)^{1/2}$ with $\varepsilon$ being the electron charge and $\mu$ the reduced effective mass. A plot of $(4/3\pi) \times (E_n - E_g)^{3/2}$ versus the index number $n$ will yield a straight line with slope $(\hbar \omega)^{-3/2}$. Therefore, the electric field ($F$) can be obtained directly from the period of the FKOs.

The surface barrier height is related to the built-in electric field by\textsuperscript{9,30}

$$V_b = Fd + kT/e + eF^2/2eN,$$  \hspace{1cm} (2)

where $d$, $k$, $T$, $e$, and $N$ represent the undoped layer thickness of the SiN$^+$ structure, the Boltzmann constant, temperature, dielectric constant, and doping concentration, respectively. The surface Fermi level $V_f$, measured from the conduction band at the surface, is equal to $V_b + V_s$,\textsuperscript{9,31} where $V_s$ represents the photovoltage induced by both the pump and probe beams.\textsuperscript{8} If both the pump and probe beams are defocused on the sample and held at sufficiently low intensities, the photovoltage induced is a small constant and can be ignored. The surface Fermi level $V_f$ is then equivalent to the surface barrier height $V_b$.

However, if the probe beam alone is defocused on the sample and maintained at sufficiently low intensity, the photovoltage and hence the surface barrier height $V_b$ become a function of the pump beam intensity only. According to current-transport theory, the photovoltage $V_s$ can be expressed as\textsuperscript{32}

$$V_s = (\eta \kappa T/e) \ln(I_{pc}/I_0 + 1),$$  \hspace{1cm} (3)

where $\eta$ represents an ideality factor,\textsuperscript{31} $I_{pc}$ equals the photocurrent density $J_{pc}$ times the surface area $A_{pc}$, simultaneously illuminated by both the pump and probe beams, and $I_0 = I_0(T)$ denotes the saturation current. The photocurrent density $J_{pc}$ comprises the drift and diffusion currents and can be expressed as\textsuperscript{34}

$$J_{pc} = \left[ eP_m \gamma (1 - R_0)/\hbar \omega \right] \left[ 1 - \exp(-\alpha L) \right]$$

$$+ aL_d \exp(-\alpha L)/(1 + aL_d),$$  \hspace{1cm} (4)

where $\gamma$ denotes the quantum efficiency, $R_0$ represents the reflectivity of the sample surface, and $\hbar \omega$ is the photon energy of the pump beam. $L$ denotes the depletion width approximately equivalent to the top layer thickness $d$, $\alpha$ represents the absorption coefficient, and $L_d$ is the diffusion length of the minority carriers. For cases in which the diffusion length significantly exceeds the penetration depth, namely, $aL_d \gg 1$, Eq. (4) reduces to

$$J_{pc} = eP_m \gamma (1 - R_0)/\hbar \omega.$$  \hspace{1cm} (5)

The saturation current $I_0(T)$ depends on the dominant current flow mechanism\textsuperscript{31} and is equal to the saturation current density $J_0(T)$ times an effective area $A_0$,\textsuperscript{17} which contributes to the current mechanism. For samples of SiN$^+$ structure, thermionic emission and diffusion are the major contributors to $J_0(T)$ and, therefore, $J_0(T)$ can be expressed as\textsuperscript{9,17,31}

$$J_0(T) = (A* T^2/(1 + BT^{3/2})) \exp[-eV_b(T)/kT],$$  \hspace{1cm} (6)

where $V_b(T)$ denotes the surface Fermi level at temperature $T$, $A*$ represents the modified Richardson constant defined as $m^* e^2/(2 \pi^2 \hbar^3)$ and $B = (k/2 \pi m^*)^{1/2}(300/\nu_0)^{35}$ where $m^*$ is the effective mass of the electron and $\nu_0$ is the thermal velocity. By substituting Eqs. (5) and (6) into Eq. (3) with $I_{pc} = A_{pc}J_{pc}$ and $I_0 = A_0I_0$, the surface barrier height is\textsuperscript{31,32}

$$V_b = V_f - (\eta \kappa T/e) \ln \left[ 1 + eP_m \gamma (1 - R_0)(1 + BT^{3/2}) \right]$$

$$\times \exp(eV_b/kT)/\hbar \omega A* T^2.$$  \hspace{1cm} (7)

where the geometry factor $r = A_0/A_{pc}$ corresponds the fraction of the surface with surface states.

At a constant temperature, the only variable in Eq. (7) is the pump beam intensity $P_m$. When the experimental surface barrier height $V_b$ as a function of pump beam intensity is least squares fitted to Eq. (7), $V_f$, $\eta$, and $r$ can be obtained from the fitting parameters. By assuming one surface state per atom at the surface,\textsuperscript{17} the surface state density $D_s$ can be calculated from $rN_0$, where $N_0$ denotes the number of atoms per unit area of the surface. However, if $P_m$ is constant and sufficiently low, the only variable in Eq. (7) is the temperature $T$. Meanwhile, when the surface barrier height as a function of temperature is least squares fitted to Eq. (7), $V_f$, $\eta$, and $r$ can be obtained from the fitting parameters and the surface state density $D_s$ can be calculated from $r$.

In the case of two surface state distributions (two pinning levels), Eq. (7) can be generalized by\textsuperscript{3,6}

$$V_b(T) = V_f - \frac{kT}{e} \ln \left[ 1 + \frac{\gamma P_m (1 - R_0)/\hbar \omega}{\left[ A* T^2/(1 + BT^{3/2}) \right] \Sigma_{i=1}^{n} F_i \exp\left( -eV_i/\hbar \omega A* T^2 \right) } \right].$$  \hspace{1cm} (8)

where $V_i$, $r_i$, $\eta_i$, and $F_i$ are the center positions (pinning positions) measured from the conduction band edge, geometry factor, ideality factor, and occupation probability, respectively, of the $i$th distribution. By assuming that the surface state distribution in energy space is a Gaussian distribution function with half width $\sigma_i$ as demonstrated in our previous investigation,\textsuperscript{5} the occupation probability $F_i$ is\textsuperscript{1}

$$F_i(T) = \int \exp[ - (E_i - V_i)^2/2\sigma_i^2 ]/\left[ \sqrt{2\pi} \sigma_i \right] dE.$$  \hspace{1cm} (9)

Additionally, the mechanism of the built-in electric field can be interpreted with a simple parallel capacitor model.\textsuperscript{1} The built-in electric field $F$ is related to the surface charge density by $Q(T) = eF$. By assuming that surface charges are uniformly distributed over the surface of the sample, Eq. (2) becomes\textsuperscript{17}
\[ V_b(T) = Q(T) d\epsilon + kT/\epsilon + Q^2(T)/2e\epsilon N^+, \]

where \( Q(T) = gN_0 \sum_{i=1}^2 n_i r_i F_i \) with \( N_0 \) representing the number of atoms per unit area of the surface. \(^1\) By simultaneously fitting the measured barrier height \( V_b(T) \) as a function of temperature to Eqs. (8) and (10), \( \eta_i, V_i, r_i \), and \( n_i \) can be obtained as the fitting parameters. The density of surface states \( D_i \) of the \( i \)th distribution can be estimated using \( D_i = r_i N_0 \).

III. APPARATUS AND EXPERIMENT

A standard arrangement of the PR apparatus was used here.\(^7\)

A He–Ne laser served as the pump beam. The probe beam consisted of a tungsten lamp and a quarter-meter monochromator combination. The probe beam was defocused on the sample and its intensity was maintained at 0.10 \( \mu \text{W/cm}^2 \). The photovoltage induced by the probe beam was thus very small and could be neglected. The detection scheme was comprised of a silicon photodetector and a lock-in amplifier. The modulated reflectance signals, \( \Delta R/R \), were processed using the lock-in amplifier and a personal computer. A detailed description of the PR spectroscopy apparatus can be found in Ref. 37. The sample studied is a molecular beam epitaxial grown \( \text{InAlAs}^+ \) structure, consisting of an \( \text{InAlAs} \) intrinsic layer (top layer) atop a 1 \( \mu \text{m} \) Si-doped, \( n \)-type \( \text{InAlAs} \) buffer layer grown on a Fe-doped semi-insulated InP substrate. The doping concentration is around \( 1.0 \times 10^{18} \text{ cm}^{-3} \).

Room temperature photoreflectance spectra of samples with various top layer thicknesses were first measured over a wide range of pump beam intensities (0.10–300.0 \( \mu \text{W/cm}^2 \)). The dependence of the surface barrier height on the pump beam intensity was deduced from the variation of the period of the Franz–Keldysh oscillations in the PR spectra. PR spectra were then measured over a wide temperature range (20 to 370 K) with the intensities of the pump beam and probe beams both kept at 0.10 \( \mu \text{W/cm}^2 \). The temperature dependence of the barrier height was again deduced from the variation of the period of the Franz-Keldysh oscillations. The photovoltage induced is very small and can be ignored.

IV. RESULTS AND DISCUSSIONS

Figure 1 displays the room temperature PR spectra of the \( \text{InAlAs}^+ \) structure measured under various pump beam intensities. All the spectra exhibit Franz–Keldysh oscillations that originate from the uniform electric fields in the intrinsic region under various pump beam intensities. Figure 2 plots \((4/3\pi)(E_n - E_p)^{3/2}\) versus the FKO extrema index \( n \) for one of the spectra displayed in Fig. 1. The solid line in Fig. 2 denotes linear fits to Eq. (1). From the slope of the straight line, the electric fields \( F \) under various pump beam intensities can be obtained from \( h \Theta = (e^2 \hbar^2 F^2 /8\mu) \). The surface barrier height \( V_b \) is then calculated using Eq. (2) and is plotted as a function of pump beam intensity in Fig. 3 for samples with various undoped layer thicknesses. The solid lines in Fig. 3 stand for the least-squares fits of the experimental data to Eq. (8). For \( \text{InAlAs} \), where \( A^* = 8.5 \text{ A/cm}^2 \text{K}^2 \), \( B = 3.2 \times 10^{-4} \text{ K}^{-3/2} \), \( \gamma = 1 \), \( N_0 = 5.8 \times 10^{14} \text{ cm}^{-2} \), and \( R_0 = 0.30 \), the fitting parameters obtained for an \( \text{InAlAs}^+ \) structure with a 1000 \( \AA \) undoped layer thickness are \( V_F = 0.70 \pm 0.02 \text{ eV} \), \( \eta = 0.80 \pm 0.05 \), and \( r = (1.0 \pm 0.5) \times 10^{-3} \). Meanwhile, the density of occupied surface states estimated from \( D_i = r N_0 \) is \((5.80 \pm 2.90) \times 10^{11} \text{ cm}^{-2} \). Table I lists these results, along with those of other samples. Our previous studies\(^7,26\) found that the surface Fermi level of \( \text{In}_{1-x}\text{Al}_x\text{As}^+ \) structures is not pinned at the midgap for an aluminum concentration of 0.42–0.57. For

FIG. 1. Room temperature PR spectra of the \( \text{InAlAs}^+ \) structure measured under various pump beam intensities.

FIG. 2. Plot of \((4/3\pi)(E_n - E_p)^{3/2}\) vs the FKO extrema index \( n \) for one of the spectra displayed in Fig. 1.
each Al composition certain ranges of top layer thickness exist within which the surface Fermi level is weakly pinned. From the dependence of the electric field and surface Fermi level on the top layer thickness, we can infer that the surface states are distributed over two separate regions within the energy band gap and that their densities are as low as \((3.51 \pm 0.15) \times 10^{11} \text{ cm}^{-2}\) for the distribution near the conduction band \((U)\) and \((4.61 \pm 0.50) \times 10^{11} \text{ cm}^{-2}\) for the distribution near the valence band \((L)\). In this work, the top layer thickness of the sample is 1000 Å. Our previous studies demonstrated that the surface Fermi level is pinned within the lower distribution. The surface state density obtained here is the surface state density of the lower distribution occupied by electrons and is comparable to the result obtained in our previous investigations. The slight discrepancy between the surface state densities obtained here and those in our previous study may be explained by the fact that the samples come from different sources.

Table I also includes the surface Fermi level, ideality factor, geometry factor, and occupied surface state density for samples with various undoped layer thicknesses obtained from the dependence of the surface barrier height on the pump beam intensity. Notably, as the thickness decreases from 2000 to 200 Å, the surface Fermi level rises from 1.09 to 0.65 eV below the conduction band edge, as illustrated schematically in Fig. 4. Meanwhile, the occupied surface state density increases from \(8.12 \times 10^{11}\) to \(14.50 \times 10^{11}\) cm\(^{-2}\). Notably, when the undoped layer thickness is below 1.0 eV, the photovoltage is very small and negligible, Fig. 5 illustrates the photovoltage calculated from the PR spectra measured at various temperatures while the total intensities of the pump and probe beams were maintained at 1.0 μW/cm\(^2\). The electric field and surface barrier heights were also deduced from the PR spectra measured at various temperatures while the total intensities of the pump and probe beams were maintained at 1 μW/cm\(^2\). In Fig. 6 the barrier heights obtained as a function of temperature are represented by.

![Image](https://example.com/image.png)

**FIG. 3.** Surface barrier height \(V_b\), calculated by Eq. (2) plotted as a function of the pump beam intensity. The solid lines represent the least-squares fits of the experimental data to Eq. (8). □, ▽, ●, ○, and ■ denote 0.02, 0.05, 0.10, 0.12, and 0.20 μm top layer thicknesses, respectively.

**FIG. 4.** Schematic diagram of the surface Fermi level position and the surface state distributions for \(\text{In}_{0.52}\text{Al}_{0.48}\text{As}\) samples. □: Unoccupied surface states; ● occupied surface state.

**TABLE I.** Surface Fermi level, ideality factor, geometry factor, and occupied surface state density obtained for samples with various undoped layer thicknesses obtained from dependence of the surface barrier height on the pump beam intensity.

<table>
<thead>
<tr>
<th>Top layer thickness (Å)</th>
<th>2000</th>
<th>1200</th>
<th>1000</th>
<th>500</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_F) (eV)</td>
<td>1.09±0.05</td>
<td>0.7±0.05</td>
<td>0.66±0.05</td>
<td>0.65±0.05</td>
<td>0.65±0.05</td>
</tr>
<tr>
<td>Geometry factor (r)</td>
<td>0.0014</td>
<td>0.0020</td>
<td>0.0020</td>
<td>0.0022</td>
<td>0.0025</td>
</tr>
<tr>
<td></td>
<td>±0.0005</td>
<td>±0.0005</td>
<td>±0.0005</td>
<td>±0.0005</td>
<td>±0.0005</td>
</tr>
<tr>
<td>Ideality factor (\eta)</td>
<td>0.8±0.0005</td>
<td>0.7±0.0005</td>
<td>0.8±0.0005</td>
<td>0.8±0.0005</td>
<td>0.9±0.0005</td>
</tr>
</tbody>
</table>
open circles. The solid line in Fig. 6 denotes the least-squares fit of the data points to both Eqs. (8) and (10). The fitting parameters obtained are \( h_1 = 1.80 \pm 0.05 \), \( V_1 = 0.99 \pm 0.02 \) eV, \( \sigma_1 = 0.08 \pm 0.01 \), \( r_1 = 0.002 \pm 0.0005 \), \( h_2 = 0.70 \pm 0.05 \), \( V_2 = 0.69 \pm 0.02 \) eV, \( \sigma_2 = 0.03 \pm 0.01 \), and \( r_2 = 0.001 \pm 0.0005 \). Table II lists these parameters. The two pinning positions or distribution centers are located 0.99 and 0.69 eV below the conduction band edge, respectively. The densities of the surface state distributions estimated from \( D_s = r N_0 \) are \( 5.80 \pm 2.90 \times 10^{11} \) cm\(^{-2}\) for the distribution near the conduction band (upper distribution) and \( 1.16 \pm 0.29 \times 10^{12} \) cm\(^{-2}\) for that near the valence band (lower distribution). These results again agree well with those obtained from the studies of pump beam intensity dependence and undoped layer thickness dependence of the surface barrier height. Table II lists all the surface state densities obtained from various approaches. Clearly, the results obtained from various techniques are consistent with each other.

V. CONCLUSION

The surface barrier height of an InAlAs surface intrinsic-\( n^+ \) structure was determined via photoreflectance spectra. The surface Fermi level and surface state densities were determined independently through the dependencies of the barrier height on temperature and pump beam intensity. The photovoltaic effect at various pump and probe beam intensities was also investigated, and indicated that the photovoltaic effect could be ignored when the pump and probe beam intensities were both maintained below 1 \( \mu W/cm^2 \). In addition, the surface states of the InAlAs were distributed over two regions within the energy band gap. These results correlate well with our previous work on measuring the surface barrier height as a function of top layer thickness.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pinning position (eV)</th>
<th>Geometry factor</th>
<th>Density of surface states (( 10^{11} ) cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( V_1 )</td>
<td>( r_1 )</td>
<td>( D_1 )</td>
</tr>
<tr>
<td>Top layer thickness(^a)</td>
<td>0.62 \pm 0.01</td>
<td></td>
<td>4.61 \pm 0.10 ( 3.51 \pm 0.10 )</td>
</tr>
<tr>
<td>Pump beam intensity</td>
<td>1.09 \pm 0.02</td>
<td>0.7 \pm 0.02</td>
<td>(1.4 \pm 0.5) \times 10^{-3} ( 1.1 \pm 0.5 ) \times 10^{-3}</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.99 \pm 0.02</td>
<td>0.69 \pm 0.02</td>
<td>(2 \pm 0.5) \times 10^{-3} ( 1 \pm 0.5 ) \times 10^{-3}</td>
</tr>
</tbody>
</table>

\(^a\)Reference 26.
ACKNOWLEDGMENT

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2See, for example, W. Mönch, in Semiconductor Surface and Interfaces, edited by G. Ertl (Springer, Berlin, 1993), and references therein.
4See, for example, J. M. Woodall, P. D. Kirchner, J. L. Freeouf, and A. C. Warren, Solid-State Electron. 33, 53 (1990), and references therein.