Molecular beam epitaxy, a Ga$_2$O$_3$ (Gd$_2$O$_3$) – GaAs structure with interface state density in the low 10$^{11}$ cm$^{-2}$ range. The density of the interface states of the Ga$_2$O$_3$ (Gd$_2$O$_3$) – GaAs structure is as low as $(1.24\pm0.14)\times10^{10}$ cm$^{-2}$. The Ga$_2$O$_3$ (Gd$_2$O$_3$) dielectric film has effectively passivated the GaAs surface. Additionally, Raman spectra were used to characterize the structural properties of the oxide films. © 2003 American Institute of Physics. [DOI: 10.1063/1.1578528]

I. INTRODUCTION

Dielectric or insulating films have played an important role in fabricating conventional and low dimensional field-effect metal–insulator conductor devices. However, for high mobility materials such as GaAs and its related compounds, which are the most commonly used in low power, high-speed devices, an insulating film with low interface state density and stable device operation is not yet available. A large density of surface or interfacial states tends to pin the Fermi level in the energy gap and results in lower gain and efficiency in solar cells and photodetectors.

Several efforts have been made to search for dielectric films such as Si$_3$N$_4$, SiO$_2$, Al$_2$O$_3$, and Ga$_2$O$_3$, deposited in combination with dry, wet and photochemical surface treatments. Recently, M. Passlack and co-workers of Bell Laboratory have reported an approach to growing, by in situ molecular beam epitaxy, a Ga$_2$O$_3$ (Gd$_2$O$_3$) – GaAs structure with interface state density in the low 10$^{10}$ cm$^{-2}$ eV$^{-1}$ range and interface recombination velocity of 4500 cm/s. They made capacitance–voltage ($C$–$V$), conductance–voltage ($G$–$V$) and steady state photoluminescence (PL) measurements to elucidate electronic interface properties.

More recently, the Bell Labs group has demonstrated enhancement-mode metal–oxide–semiconductor field-effect transistors (MOSFETs) with inversion, using Ga$_2$O$_3$ (Gd$_2$O$_3$) as the gate dielectric and a conventional ion implantation process. and doping concentration during the last three 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. In our previous report, we presented results of our studies on the electronic properties of the oxide–semiconductor interface by photoreflectance. Four samples, air-, Al$_2$O$_3$–, Ga$_2$O$_3$–, and Ga$_2$O$_3$ (Gd$_2$O$_3$)–GaAs (bare GaAs surface) were studied. From the observed Franz–Keldysh oscillations (FKOs) of the PR spectra we were able to estimate the intervalence electric fields and the densities of interfacial states for air-, Al$_2$O$_3$–, and Ga$_2$O$_3$–GaAs interfaces. The density of interfacial states of Ga$_2$O$_3$ (Gd$_2$O$_3$)–GaAs was estimated from the low field limit criterion in photoreflectance spectroscopy, since no FKOs appear in PR spectra within the low field limit.

This study determines the barrier heights across the interfaces and the densities of interfacial states of air-, Al$_2$O$_3$–, Ga$_2$O$_3$–, and Ga$_2$O$_3$ (Gd$_2$O$_3$)–GaAs from the PR intensity as a function of the pump power density. Moreover, Raman spectroscopy was also used to characterize the structural characteristics of the epitaxial films. A coherent picture can be drawn from results obtained from previous and present PR studies, Raman spectroscopy and other studies.

II. THEORY

In PR, the electric field of the sample is modulated through changes in the surface photovoltage induced by the absorption of photons with energy above the band gap energy. When an electric field is applied to a sample, the electrons and holes are accelerated by the field. The line shape of the PR signal, $\Delta R/R$, is directly related to the perturbed dielectric function. In the low field limit, $\hbar \Omega^3/\Gamma^3 < 1/3$, the line shape of the PR spectrum can be fitted to
\[ \Delta R/R = \text{Re}[A e^{i\theta}(E - E_g + i\Gamma)^{-\ell}], \]

where \( A \) is the amplitude, \( \theta \) the phase angle, \( E \) the incident photon energy, \( E_g \) the interband transition energy, \( \Gamma \) the broadening parameter, \( \ell \) a parameter depending on the type of critical point (\( \ell = 5/2 \) for a three-dimensional critical point), and \( \hbar \Omega \) is the electro-optical energy defined by

\[ (\hbar \Omega)^3 = (\hbar F e)^2/2\mu, \]

where \( F \) is the electric field and \( \mu \) is the reduced interband electron and heavy hole pair effective mass in the direction of the electric field. For a moderate electric field, the PR spectrum exhibits a series of oscillations (FKOs). The asymptotic expression for the FKO line shape is given by \(^{31-33}\)

\[ \Delta R/R \sim E^{-2}(E - E_g)^{-1} \exp\left(-\frac{\Gamma(E - E_g)1/2}{(\hbar \Omega)^{3/2}}\right) \times \cos\left[\frac{2}{3}\left(\frac{E - E_g}{\hbar \Omega}\right)^{3/2}\right], \]

where \( \chi \) is an arbitrary factor. The extremes of the FKO in Eq. (3) occur when

\[ n\pi = (4/3)(E_n - E_g)/\hbar \Omega)^{3/2} + \chi, \quad n = 1, 2, 3, \ldots \]

where \( n \) represents the index number of the FKO extremes. A plot of \((4/3\pi)(E_n - E_g)^{3/2}\) 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 mechanism of the built-in electric field can be interpreted by a simple model of the parallel plate capacitor. The band bending region which supplies the PR signal is sandwiched between the negative charges in the interface states (surface states for an air-GaAs structure) and the positive charges in the thin depletion layer in \( n \)-type GaAs. The electric field of the capacitor is given by

\[ F = \sigma_r/\varepsilon_0 = eD_r/\varepsilon_0, \]

where \( \sigma_r, e, \varepsilon_0, e \) and \( D_r \) represent the charge density, relative dielectric constant, free space permittivity, free electron charge and density of the occupied interfacial states, respectively. Once the electric field is obtained from the FKOs, the interfacial charge density \( \sigma_r \) and thus the interfacial state density \( D_r \) can be calculated from Eq. (5). For samples with built-in electric field within the low field limit, their PR spectra do not exhibit Franz–Keldysh oscillations. The built-in electric fields can only be estimated from the low field limit criterion, \( [\hbar \Omega]^{3/2}\Gamma^{1/2} < 1/3 \). The only information provided by the PR spectra is that the built-in electric field and surface or interfacial state densities are smaller than those calculated from \( [\hbar \Omega]^{3/2}\Gamma^{1/2} = 1/3 \).

An alternative approach can be taken to derive precisely the surface or interfacial state densities independent of whether the built-in electric fields are below the low field limit or in the moderate field regions. Under low-intensity low-frequency modulation, the PR intensity \( \Delta R/R \), at fixed probe wavelength, is directly proportional to the modulating photovoltage \( (V_s) \) induced by the pump beam, and is given by \(^{34-38}\)

\[ \Delta R/R \approx \eta kT/e \ln(I_{pc}/I_0 + 1), \]

where \( \eta \) is an ideality factor; \(^{39}\) \( I_{pc} \) is equal to the photocurrent density \( J_{pc} \) times the surface area \( A_{pc} \) simultaneously illuminated by both the pump and probe beams, and \( I_0 = I_0(T) \) represents the saturation current, which depends on the dominant current flow mechanism \(^{40}\) and is equal to the saturation flow density \( J_0(T) \) times an effective area \( A_0 \), which effectively contributes to the current mechanism. The photocurrent density \( J_{pc} \) includes the drift and diffusion current densities. According to current–transport theory applied to the case in which the diffusion length is much larger than the penetration depth of the pump beam, \( J_{pc} \) can be written as \(^{37,38,41}\)

\[ J_{pc} = eP_m \gamma(1 - R_0)/h \omega, \]

where \( P_m \) is the pump beam power density, \( \gamma \) is the quantum efficiency, \( R_0 \) is the reflectivity of sample surface and \( h \omega \) is the photon energy of the pump beam.

Thermionic emission and diffusion are the main contributions to \( J_0(T) \) so \( J_0 \) can be expressed as \(^{14,25,38,40}\)

\[ J_0(T) = [A^* T^2/(1 + BT^2)] \exp[-eV_b(T)/kT], \]

where \( A^* \) is the modified Richardson constant defined as \( m^* e k^2/(2\pi^2 h^3 \times 3) \); \( V_b \) is the barrier height across the interface or surface barrier height on the bare surface, and \( B = (k/2\pi m^*)^{1/2}(300/\nu_0)^{3/2} \) where \( m^* \) is the effective mass of the electron. Substituting Eqs. (7) and (8) into Eq. (6) with \( I_{pc} = A_{pc} J_{pc} \) and \( I_0 = A_0 J_0 \) yields a PR intensity of

\[ \Delta R/R \sim \eta kT/e \ln[1 + eP_m \gamma(1 - R_0)(1 + BT^2)] \times \exp[eV_b/kT]/h \omega r A^* T^2, \]

where \( r = A_0/A_{pc} \) is defined as the geometric factor introduced by Yin et al. \(^{26}\)

At constant temperature, the only variable in Eq. (9) is the pump beam power density \( P_m \). When experimental values \( \Delta R/R \) at various pump beam intensities are least squares fitted to Eq. (9), \( V_b, \eta \) and \( r \) can be obtained from the fitting parameters. The density of surface or interfacial states is then calculated from \( rN_0 \) where \( N_0 \) is the number of atoms per unit area of the surface.

**III. EXPERIMENT**

The samples were grown using an ultrahigh vacuum (UHV) multiple-chamber molecular beam epitaxy (MBE) system. A typical growth sequence entailed different oxide films being deposited on a 1.5 \( \mu \text{m} \) \( n \)-type GaAs buffer layer \((1.6 \times 10^{16} \text{ cm}^{-2})\) which had previously been grown on a highly doped \( n \)-type (100) GaAs substrate. The oxide films, \( \text{Al}_2\text{O}_3 \), \( \text{Ga}_2\text{O}_3 \), and \( \text{Ga}_2\text{O}_3\text{(Gd}_2\text{O}_3)\)–GaAs, were deposited using molecular beams of aluminum oxides, gallium oxides, and a mixture of gallium oxides and gadolinium oxides, respectively. Single crystals of \( \text{Al}_2\text{O}_3 \), \( \text{Ga}_2\text{O}_3 \), and \( \text{Gd}_2\text{Ga}_2\text{O}_12 \) were used as source materials and evaporated by the e-beam technique. According to the work reported by Passlack et al. \(^{10}\) the use of \( \text{Gd}_2\text{Ga}_2\text{O}_12 \) was motivated by the unavailability of single \( \text{Ga}_2\text{O}_3 \) crystal and led to the success-
ful deposition of gallium oxide molecules that formed extremely uniform nonstoichiometric Ga₂O₃(Gd₂O₃) films on GaAs. Samples with different dielectric film materials and thickness are listed in Table I.

A standard PR apparatus was used in this study. The probe beam consisted of a tungsten lamp and a 1/4 m monochromator. A He–Ne laser served as the pump beam. The detection scheme consisted of a Si photodetector and a lock-in amplifier. The probe and pump beams were defocused onto the sample to reduce the photovoltaic effect. All measurements were performed at room temperature and modulation frequency of 200 Hz. The dependence of the PR intensity on the pump beam intensity was measured with the wavelength of the probe beam fixed at one of the two major extrema of the PR spectrum. The pump beam intensity, controlled by a gradient neutral density filter, was varied from 0.3 to 1000 μW/cm². Data were measured by a computerized acquisition system.

Raman scattering experiments were performed in backscattering geometry on sample surfaces using an Ar⁺-ion laser. Raman spectra of III–V compound semiconductors with zinc-blende crystal structure generally show two peaks. The lower-frequency peak corresponds to transverse optical (TO) phonons while the higher peak corresponds to longitudinal optical (LO) phonons. Only LO phonons appear in the (100) backscattering direction, and only TO phonons appear in the (110) direction, while both appear in the (111) direction.43,44 The laser output power was fixed at 100 mW so as to prevent excess heating of the samples and was focused onto the samples by a cylindrical lens. The light scattered was analyzed using a standard double-grating spectrometer in photon-counting mode, and the spectral resolution was better than 2 cm⁻¹.

### IV. RESULTS AND DISCUSSION

Figure 1 displays the PR spectra for all samples at room temperature measured at a pump beam power of 1 μW/cm². The spectra of air-, Al₂O₃–, and Ga₂O₃–GaAs samples exhibit FKO features (labeled A–D in Fig. 1) with different periods above the energy gap of GaAs (1.42 eV). They indicate that electric fields of various strengths exist in the interface regions of the samples and that the strengths of these fields are above the low field limit. In Fig. 2, (4/3π)(Eₙ₋₁₋Eₙ)³/₂ is plotted as a function of the extreme index n in the spectra. The solid lines are linear fits to Eq. (4). The slope of the solid line yields the electro-optic energy hΩ, which in turn gives the built-in electric field F. The effective masses of the electrons and heavy holes in GaAs used here are 0.065 and 0.34m₀, respectively, where m₀ is the free electron mass. Once the electric field is determined from the FKOs, the interfacial charge density nᵢ, and thus the occupied interfacial state density Dᵢ, can be calculated from Eq. (5).

![FIG. 1. PR spectra of samples of air-, Al₂O₃–, Ga₂O₃–, and Ga₂O₃(Gd₂O₃)–GaAs at room temperature.](image)

![FIG. 2. Quantity (4/3π)(Eₙ₋₁₋Eₙ)³/₂, as a function of index n of the FKO extrema.](image)

<table>
<thead>
<tr>
<th>Dielectric film</th>
<th>Thickness (Å)</th>
<th>F (kV/cm)</th>
<th>Dᵢ (10¹¹ cm⁻² eV⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>48</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>700</td>
<td>44</td>
<td>2.2</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>600</td>
<td>38</td>
<td>1.9</td>
</tr>
<tr>
<td>Ga₂O₃(Gd₂O₃)</td>
<td>&lt;21¹</td>
<td>&lt;1.0</td>
<td></td>
</tr>
</tbody>
</table>

*Estimated from the low field criterion |hΩ|/|Γ|<1/3.

<table>
<thead>
<tr>
<th>Sample Structure</th>
<th>Oxide Film Thickness</th>
<th>Values of the Interfacial Charge Density nᵢ</th>
<th>Values of the Interfacial State Density Dᵢ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-GaAs</td>
<td>48</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃-GaAs</td>
<td>700</td>
<td>44</td>
<td>2.2</td>
</tr>
<tr>
<td>Ga₂O₃-GaAs</td>
<td>600</td>
<td>38</td>
<td>1.9</td>
</tr>
<tr>
<td>Ga₂O₃(Gd₂O₃)-GaAs</td>
<td>&lt;21¹</td>
<td>&lt;1.0</td>
<td></td>
</tr>
</tbody>
</table>

The spectra of air-, Al₂O₃–, Ga₂O₃–, and Ga₂O₃(Gd₂O₃)–GaAs estimated from Eq. (5) is less than 1.0×10¹¹ cm⁻². Table I lists the results for all samples.
Figure 3 presents the PR spectra of all samples at room temperature measured at various pump power densities. Figure 4 depicts the PR intensity ($\Delta R/R$) as a function of pump power density for all samples. For each sample, the PR signal was measured with the probe beam wavelength fixed at the major extreme prior to the band gap energy in the PR spectra. The solid lines are the least-squares fits obtained using Eq. 9. For GaAs samples, when $A^* = 8.0$ A/cm$^2$ K$^{-2}$, $B = 3.3 \times 10^{-4}$ K$^{-3/2}$, $\gamma = 1$, $N_0 = 6.3 \times 10^{14}$ cm$^{-2}$, and $R_0 = 0.34$, the fitting parameters are $V_b$, $\eta$, and $r$. Table II lists the fitting parameters obtained and the densities of interfacial states $D_i$ calculated from $rN_0$. The densities of interfacial states determined by both approaches are comparable and are in the low $10^{11}$ cm$^{-2}$ range for air-, Al$_2$O$_3$–, and Ga$_2$O$_3$–GaAs. For Ga$_2$O$_3$(Gd$_2$O$_3$)–GaAs, $D_i$ is as low as $(1.24 \pm 0.14) \times 10^{10}$ cm$^{-2}$, implying that the GaAs surface is effectively passivated by the Ga$_2$O$_3$(Gd$_2$O$_3$) dielectric film. The results are also consistent with those reported by Passlack et al. who determined $D_i$ from capacitance–voltage measurements in quasistatic/high frequency modes. Hong and co-workers attributed the low $D_i$ in Ga$_2$O$_3$(Gd$_2$O$_3$)–GaAs to the formation of bonding between Gd$_2$O$_3$ and GaAs.

Figure 5 shows Raman spectra of all samples. Each spectrum shows a strong peak at 290 cm$^{-1}$ and a weak peak at 266 cm$^{-1}$ that represent the LO and TO modes, respectively. As stated earlier, only the LO mode is allowed in $\sim$100 oriented material. However, a peak associated with the TO mode is also observed, probably because of a slight substrate misorientation or imperfection or perhaps a small experimental deviation from backscattering. This phenomenon was also observed with other (100) oriented III–V semiconductors.

Each peak in the Raman spectra of all of the samples was fitted to a Lorentzian line shape to determine its amplitude, position, and full width at half maximum (FWHM). The solid lines in Fig. 5 represent the theoretical fits. Table III lists the results for LO modes. The results for TO modes are not considered here since they follow from substrate misorientation or imperfection of the substrate, or a small experimental deviation from backscattering. Notably, Ga$_2$O$_3$(Gd$_2$O$_3$)–GaAs, which has the lowest interface state density, has the lowest Raman peak intensity and the greatest

**TABLE II.** Interfacial barrier height, geometric factor, and densities of interfacial states $D_i$ derived from the PR intensity as functions of the pump power density.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_b$ (eV)</th>
<th>$r$</th>
<th>$D_i$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-GaAs</td>
<td>0.52±0.05</td>
<td>$(3.75\pm1.34)\times10^{-4}$</td>
<td>$(2.36\pm0.84)\times10^{11}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$–GaAs</td>
<td>0.44±0.05</td>
<td>$(2.60\pm1.18)\times10^{-4}$</td>
<td>$(1.64\pm0.74)\times10^{11}$</td>
</tr>
<tr>
<td>Ga$_2$O$_3$–GaAs</td>
<td>0.41±0.07</td>
<td>$(1.66\pm0.15)\times10^{-4}$</td>
<td>$(1.05\pm0.09)\times10^{11}$</td>
</tr>
<tr>
<td>Ga$_2$O$_3$(Gd$_2$O$_3$)–GaAs</td>
<td>0.4±0.05</td>
<td>$(1.97\pm0.22)\times10^{-5}$</td>
<td>$(1.24\pm0.14)\times10^{10}$</td>
</tr>
</tbody>
</table>
FWHM, because Ga$_2$O$_3$(Gd$_2$O$_3$) film on GaAs is a nanocrystalline film that consists of small grains of either Ga$_2$O$_3$ or Gd$_2$O$_3$, whereas Al$_2$O$_3$ and Ga$_2$O$_3$ films are amorphous and polycrystalline, respectively, with each a single oxide with preferred orientation. A nanocrystalline film of two different oxide grains usually has a less intense wider Raman peak. In addition, Hong et al. found, using reflection high energy electron diffraction (RHEED) and x-ray diffraction, that the first few molecular layers of Ga$_2$O$_3$(Gd$_2$O$_3$) oxides grown on GaAs include only Gd$_2$O$_3$ single crystals while the layers grown subsequently include a mixture of Ga$_2$O$_3$ and Gd$_2$O$_3$ oxides. Their conclusions are consistent with the features of the Raman spectra obtained herein, since the existence of Gd$_2$O$_3$ single crystal epitaxial film further reduces the intensity and increases the width of the Raman peak.

**TABLE III.** Amplitude, center position, and FWHM of the LO mode of the Raman spectra at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vibration mode: $\nu_{LO}$</th>
<th>Amplitude</th>
<th>Center (cm$^{-1}$)</th>
<th>Half width (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-GaAs</td>
<td></td>
<td>259.1</td>
<td>289.1</td>
<td>4.7</td>
</tr>
<tr>
<td>Al$_2$O$_3$–GaAs</td>
<td></td>
<td>236.0</td>
<td>289.1</td>
<td>5.7</td>
</tr>
<tr>
<td>Ga$_2$O$_3$–GaAs</td>
<td></td>
<td>324.8</td>
<td>289.2</td>
<td>6.7</td>
</tr>
<tr>
<td>Ga$_2$O$_3$(Gd$_2$O$_3$)–GaAs</td>
<td></td>
<td>74.1</td>
<td>290.7</td>
<td>22.2</td>
</tr>
</tbody>
</table>

**V. CONCLUSIONS**

The contactless nondestructive technique of photoreflectance was employed to determine the barrier heights and densities of interfacial states of a series of oxide-GaAs structures. In contrast in the authors’ previous report, which estimated the interfacial state densities by assuming that the band bending region across the interface was a parallel capacitor, this study accurately determines the interfacial state density from the PR intensity as a function of the pump power density. The densities of interfacial states obtained match the results of our previous report and also those obtained from capacitance–voltage measurements in quasistatic/high frequency modes. The oxide-GaAs structures fabricated by in situ molecular beam epitaxy were found to exhibit low interfacial state densities, in the low $10^{11}$ cm$^{-2}$ range. The density of interface states of Ga$_2$O$_3$(Gd$_2$O$_3$)–GaAs is as low as $(1.24\pm0.14) \times 10^{10}$ cm$^{-2}$. The Ga$_2$O$_3$(Gd$_2$O$_3$) dielectric film has effectively passivated the GaAs surface. Moreover, Raman spectra were used to characterize the structural properties of the oxide films.

**ACKNOWLEDGMENT**

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25 See, for example, J. M. Woodall, P. D. Kirchner, J. L. Freeouf, and A. C. Warren, Solid-State Electron. 33, 53 (1990), and references therein.