Changing photoluminescence intensity from GaAs/Al$_{0.3}$Ga$_{0.7}$As heterostructures upon chemisorption of SO$_2$

J. F. Geisz$^a$ and T. F. Kuech
Department of Chemical Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706

A. B. Ellis
Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706

(Received 24 February 1994; accepted for publication 25 October 1994)

Chemisorption of SO$_2$ gas molecules onto photowashed GaAs surfaces results in a change in the density of charge at the surface, giving rise to a measurable change in the charge distribution within the semiconductor. We consider the development of a novel semiconductor chemical sensor based on this phenomenon. The intensity of photoluminescence (PL) from metalorganic vapor phase epitaxy grown GaAs/Al$_{0.3}$Ga$_{0.7}$As structures at 300 K is used to detect this change in charge distribution. The doping densities and layer thicknesses within these heterostructures are shown to have a profound influence on the relative magnitude of PL intensity and its sensitivity to changes in the density of surface charge brought about by chemisorption of SO$_2$. New analytical and finite element method (FEM) numerical models are derived to quantitatively predict the effect of changing surface charge on the PL intensity from finite thickness heterostructure layers. The PL response from these heterostructures is shown to follow the trends predicted by these models and suggests that the adsorption of SO$_2$ from a 0.6 mol % mixture of SO$_2$ in N$_2$ results in a reduction in the negative surface charge density by $9 \times 10^9$ to $2 \times 10^{10}$ cm$^{-2}$. Simultaneous changes in surface recombination rates due to adsorption are shown (using the FEM model) to have no effect on the PL intensity from the structures studied here. The results are applied to the improvement of signal characteristics from a potential chemical sensor device. © 1995 American Institute of Physics.

INTRODUCTION

Interactions of semiconductor surfaces with chemical ambients have long been known to affect the bulk electrical properties of semiconductor devices. This has been a problem in most electrical devices, requiring isolation of the semiconductor from changing ambients through packaging. We propose to use this effect to create semiconductor chemical sensing devices. The chemical sensitivity at the surface of semiconductors coupled with their useful electrical and optical properties make them well suited for use as chemical sensors.

Midgap electrical states existing at semiconductor surfaces or interfaces result in a bending of the semiconductor electrical energy bands in a region near that interface. Typically a depletion region will exist at the surface of a semiconductor. Changes in the extrinsic surface state density due to the chemisorption of gas molecules can result in a change in the density of charged states at the surface and, thus, the thickness of such a surface depletion region. The change in the density of surface charge is roughly proportional to the density of chemisorbed gas molecules, which, in turn, is related to the gas-phase partial pressure of the gas species by an adsorption isotherm. Therefore, the partial pressure of a gas-phase species that chemisorbs to a semiconductor surface may be inferred by measuring the change in the surface depletion width. This phenomenon may be used as the basis for a novel semiconductor chemical sensor device.

Measurement of photoluminescence (PL) intensity from direct band gap semiconductors has been found to be a good probe of this depletion region at a free surface. The "dead-layer model" and a more sophisticated model by Mettler have been presented to relate the surface depletion width to the PL intensity from a semi-infinite semiconductor crystal. Mettler's model has been shown to reduce to the dead-layer model under certain common conditions. This dead-layer model has been successfully used to estimate changes in the depletion width caused by adsorption of gaseous amines and boranes onto etched n-CdSe through PL intensity data. These measurements were then used to calculate Langmuir adsorption isotherm equilibrium constants.

The extremely high density of extrinsic surface states on GaAs, resulting in "Fermi level pinning" at the surface, severely impacts GaAs field-effect transistor performance and development, and suppresses the electrical sensitivity of GaAs surfaces to chemisorption. Attempts to "unpin" the Fermi level of GaAs surfaces have met various levels of success. Photowashing, sulfide passivation, and thin epitaxial Si interlayers have all been found to reduce the density of GaAs interface states.

The surface of GaAs becomes highly sensitive to changes due to chemisorption of gases when the Fermi level is unpinned. Wilsens et al. observed the PL intensity from photowashed and sulfide-passivated GaAs to be extremely sensitive to exposure to air. Meyer also observed a PL intensity dependence from photowashed, etched, and sulfide-passivated GaAs on gas-phase concentrations of NH$_3$ and SO$_2$.

We report the dependence of PL intensity from photowashed GaAs layers in GaAs/Al$_{0.3}$Ga$_{0.7}$As heterostructures on the chemisorption of SO$_2$. The effects of the layer thick-
nessec and doping levels in these heterostructures have a profound influence on the PL intensity and its dependence on SO₂ concentration. We have extended Mettler’s analytical model to the case of semiconductor layers of finite thickness to quantitatively understand these effects. Further, we have developed a finite element method (FEM) numerical code to model the PL intensity from complex heterostructures that fail to satisfy the assumptions of the analytical model. This FEM model is useful for directly understanding the effects of changing surface recombination velocities on the PL intensity and for determining when the assumptions of the analytical model will hold. The predictions of these models are substantiated by the trends of the experimental results and may be applied to the engineering of a novel semiconductor chemical sensor for optimum sensor signal characteristics.

PL INTENSITY FROM HETEROSTRUCTURES

PL is a process whereby incident light is absorbed by a semiconductor and re-emitted at different wavelengths characteristic of the electronic energy levels of the semiconductor. At low temperatures, PL spectra are used to measure the energy levels of shallow impurities and excitons within a semiconductor. Near room temperature, only a broad PL peak centered at the band-gap energy can be discerned. The relative intensity of this room temperature PL peak is modeled here as a function of heterostructure geometry and surface charge (or surface potential).

When N photons/(cm² s) of wavelength λ, are incident on a semiconductor with an optical absorption coefficient αₑ(λ), the number of photons/(cm³ s) that are absorbed at a given depth x is

\[ G(x) = (1 - R)Nαₑe^{-αₑx}, \]  

where R is the reflectivity of the surface. Each absorbed photon with energy greater than the band gap of the semiconductor may produce an electron-hole pair. The photogenerated excess carriers are transported through the semiconductor due to carrier concentration gradients and electric fields until they recombine either radiatively or nonradiatively. Upon radiative recombination, a photon with the energy of the conduction band at an arbitrary point and the quantum efficiency, \( \eta \), is given off, contributing to the PL intensity

\[ e^- + h^+ \rightarrow hν_p. \]  

This recombination reaction is first order in \( n \) and \( p \), the densities of electrons and holes, respectively. After subtraction of the reverse reaction due to thermal generation, we find the net rate of radiative recombination [photons emitted/(cm³ s)],

\[ U = r(n_eΔp + p_eΔn + ΔpΔn), \]  

where \( r \) is the rate constant for reaction (2), \( Δp \) and \( Δn \) are the excess carrier densities, and \( n_e \) and \( p_e \) are the equilibrium carrier densities. In n-type semiconductors, the radiative recombination rate is usually given in terms of a minority carrier lifetime, \( τ_e \), as \( U = Δp/τ_e \). For consistency, we consider the equations for n-type regions, though p-type is completely analogous. Since the equilibrium minority carrier density \( p_e \) is usually very small, the second term of Eq. (3) may be neglected and \( τ_e = [r(n_e + Δn)]^{-1} \). Further, for low intensity exciting light, \( Δn \ll n_e \) and the last term may be treated as a perturbation or neglected altogether.

The intensity of PL is proportional to the integral of the radiative recombination rate in the regions with band gap \( hν_p \) that does not get reabsorbed,

\[ \text{PL} \propto \int \frac{Δp(x)}{τ_e(n_e)} e^{-αₑx} dx, \]  

where self-absorption of emitted photons is considered in the term containing \( αₑ \), the optical absorption coefficient of the emitted light, and the proportionality constant is related to geometric factors and the quantum efficiency.

The radiative lifetime \( τ_e \) may also be expressed as a function of position by solving for the electron distribution \( n_e(x) \). We may express the equilibrium electron density in terms of the negative electric potential \( φ \) or the Fermi energy \( E_F \) by

\[ n_e = n_b \exp \left( -\frac{qφ}{kT} \right) = N_c \mathcal{F}_{1/2} \left( \frac{E_F - E_c}{kT} \right), \]  

where \( q \) is the elemental charge, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( n_b \) is the electron density in a charge neutral bulk in which \( φ = 0 \), \( N_c \) is the effective density of states, \( E_c \) is the conduction band energy, and \( \mathcal{F}_{1/2}(φ) \) is the Fermi–Dirac integral of order 1/2. Thus, the PL intensity may be calculated by solving for the potential distribution, \( φ(x) \), and the excess hole distribution, \( Δp(x) \). For moderate excitation powers, the photogenerated carriers do not significantly change the charge distribution through the semiconductor and the solution of the two distributions may be solved independently.

POTENTIAL DISTRIBUTION

The solution for the potential distribution within a semiconductor is equivalent to the solution for the bend bending, since the potential may be expressed as a direct function of the electron energy by solving Eq. (5). In the case of nondegenerate semiconductors, \( qφ(x) = E_c(x) - E_b \) where \( E_c(x) \) is the energy of the conduction band at an arbitrary point and \( E_b \) is that energy in the charge neutral bulk. The equilibrium potential distribution may be calculated from Poisson’s equation

\[ \frac{d^2φ}{dx^2} = \frac{ρ(φ)}{ε_iε_0}, \]  

in each region of material \( i \) with dielectric constant, \( ε_i \), in which the charge distribution is given by \( ρ = q(p_e - n_e + \Delta p_+ - \Delta p_−) \). The individual charge densities are determined by Fermi–Dirac statistics [e.g., Eq. (5)].

At the interface between different layers in a heterostructure, a boundary condition is given by a discontinuity of potential,
The distribution of photogenerated excess holes through a semiconductor layer is described by the general transport equation\textsuperscript{14,16}

\[
\frac{\partial \Delta p}{\partial t} = D_p \frac{\partial^2 \Delta p}{\partial x^2} + \mu_p \frac{\partial}{\partial x} \left[ \mathcal{E}(x) \Delta p \right] - \frac{\Delta p}{\tau_p(x) + \tau_w},
\]

where \( D_p \) is the hole diffusion coefficient, \( \mu_p \) is the hole mobility, \( \mathcal{E}(x) = d\varphi/dx \) is the electric field, and \( \tau_p \) is the hole lifetime given by

\[
\frac{1}{\tau_p} = \frac{1}{\tau_r} + \frac{1}{\tau_w},
\]

\( \tau_w \) is the nonradiative lifetime due to recombination through deep-level traps or Auger processes.

Surface and interface states often exist in midgap and are a common nonradiative recombination pathway. The flux of holes to the surface due to surface recombination is usually given in terms of a surface recombination velocity, \( s \),

\[
\frac{1}{s} \left| j_p \right|_{\text{interface}} = s D_p \Delta p \left|_{\text{interface}}. \right.
\]

\( s \) is an interfacial recombination velocity. Similarly, an interfacial recombination velocity will describe the recombination between layers. The value of this recombination velocity is dependent on the density and energy of the interface states in either of the above cases. Excess carriers may also be transported across junctions but we consider here heterojunctions with a large potential barrier.

We have written a FEM code to solve the steady-state differential equation for the excess hole distribution. The same element scheme used in the solution for the potential was used here. The radiative lifetime \( \tau_r(x) \) and the electric field \( \mathcal{E}(x) \) were determined from the solution of the potential distribution. Calculated results of the photogenerated minority carriers in a typical structure under study are also shown in Fig. 1. Values of \( \tau_r \) and \( D_p \) were taken from the literature\textsuperscript{19} as a function of doping density. The recombination velocity was taken to be 100 cm/s at the heterojunction and infinity at the surface. Notice that even with an infinite surface recombination velocity, a significant density of photogenerated holes may exist in the depletion region at steady state. The effects of changing surface recombination velocity will be discussed later. The integration in Eq. (4) was computed numerically using the trapezoidal rule to calculate the relative PL intensity.

\section*{ANALYTICAL SOLUTION}

Analytical models of the PL intensity from a semi-infinite semiconductor have previously been derived by Hollingsworth and Sites\textsuperscript{3} and Mettler.\textsuperscript{2} In both derivations, the surface depletion region is assumed to emit no PL and is thus said to be a dead layer. This assumption is justified by the fact that the minority carrier lifetime in the depletion region is significantly greater than in the bulk due to the depletion of majority carriers. Additionally, the photogenerated excess carriers in the region are quickly swept away by the electric field. While Hollingsworth and Sites assumed that all of the carriers generated in the charge neutral region away from the dead layer eventually contributed to the PL intensity, Mettler solved for the excess minority carrier distribution in the charge neutral bulk of a semi-infinite semiconductor and

\[ J. \text{Appl. Phys.}, \text{Vol. 77, No. 3, 1 February 1995} \]
compensated for self-absorption as in Eq. (4). In this section, we derive an analytical expression for the PL intensity from a semiconductor layer of finite thickness.

Poisson’s equation (6) may be solved analytically near the surface by assuming a rectangular charge distribution in the depletion region and complete impurity ionization. This results in quadratic band bending in the depletion region of width,

\[ w = \frac{N_d}{N_x - N_a}. \]  

(12)

where \( N_x \) is the density of surface charge, \( N_a \) is the acceptor density, and \( N_d \) is the donor density.

Band bending near an \( n-n \) heterojunction results in an accumulation region on one side and a depletion region on the other. The width of the accumulation region is characterized by the Debye length while the width of the depletion region may be estimated again using the assumption of complete ionization within the depletion region. In the following derivation, the widths of the heterojunction space-charge region within the layer of interest will be represented by \( x_h \).

The band bending at the \( n-n \) heterojunction as calculated by the FEM analysis may also be seen in Fig. 1. We consider PL emission only from the charge neutral region of thickness, \( t - w - x_h \), between the two space-charge regions. PL from the depletion regions is neglected for the reasons given previously. PL from the accumulation region is neglected only because the excess carriers are swept away by the electric field.

Since the equilibrium potential is constant in the charge-neutral region, the radiative lifetime \( \tau_r \) may be taken as a constant in Eq. (4). The electric field in this region is identically zero, so the drift term in Eq. (9) is eliminated.

Mettler defined an empirical “virtual” surface recombination velocity \( S_0 \) at the edge of the surface depletion region analogous to the surface recombination velocity of Eq. (11) to define the boundary conditions for the domain of interest,

\[ D_p \frac{d\Delta p}{dx} \bigg|_w = S_0 \Delta p \bigg|_w. \]  

(13)

It includes effects from transport in the space-charge region as well as the recombination at the actual surface. We also define a virtual interface velocity \( S_h \) at the edge of the heterojunction space-charge region in a similar manner.

Making the transport Eq. (9) dimensionless at steady state and using the virtual recombination velocities for boundary conditions results in the differential equation,

\[ \frac{1}{\alpha^2} \frac{d^2 P}{dz^2} - P = e^{-\alpha z}, \quad 0 \leq z \leq 1, \]  

subject to the boundary conditions

\[ \frac{dP}{dz} \bigg|_{z=0} = -\alpha_1 P \bigg|_{z=1} = 0, \]  

(14)

by making the following definitions

\[ a = \frac{(t-x_h) - w}{L_p}, \quad b = \alpha x_p, \]  

\[ \beta_0 = S_h \beta_0 / D_p, \quad \beta_1 = S_h \beta_1 / D_p, \]  

\[ P = \frac{-\Delta p D_p}{N(1-R) L_p} e^{\alpha_0 w}, \]  

where \( L_p = \sqrt{D_p / \rho} \) is the hole diffusion length, and \( S_0 \) and \( S_h \) are the surface and heterojunction interfacial recombination velocities, respectively. The solution of Eq. (14) subject to Eqs. (15) and (16) is

\[ P = f_1 e^{-az} + f_2 e^{\alpha z} + f_3 e^{-\alpha z}, \]  

(18)

where

\[ f_1 = \frac{1}{\beta_0^2 - 1}, \]  

\[ f_2 = \frac{(b + \beta_0)(1 + \beta_0) e^{-a} - (\beta_1 + b)(1 + \beta_0) e^{-ab}}{(b^2 - 1)((1 - \beta_0)(1 + \beta_0) e^{-a} - (\beta_1 + 1) e^{-ab})}, \]  

\[ f_3 = \frac{(b - \beta_0)(1 + \beta_0) e^{-a} - (\beta_1 - b)(1 + \beta_0) e^{-ab}}{(b^2 - 1)(1 + \beta_0)}. \]  

(20)

The intensity of the PL is calculated by integrating Eq. (4) from \( z = w \) to \( z = w + t \) resulting in

\[ PL \propto -N(1-R) \frac{\alpha x_p}{\tau_r} e^{(\alpha x_p - \alpha_0 w) \frac{1}{\beta_0} \left( 1 - \frac{e^{-(d + 1) z}}{d + 1} \right)} + f_2 \left( 1 - \frac{e^{-d z}}{d + 1} \right) + f_3 \left( 1 - \frac{e^{-(d + 1) z}}{d + 1} \right), \]  

(22)

where \( d = \alpha_0 L_p \). This solution reduces to Eq. (10) in Ref. 2 as the thickness of the active region, \( t - x_h - w \), becomes much larger that the diffusion length (i.e., \( a \to \infty \)).

On the accumulation side of an \( n-n \) heterojunction, \( \beta_1 \) will be very small since the direction of the electric field in the accumulation region will tend to inhibit transport of holes out of the neutral region. This assumption is shown to be good from the FEM results presented in Fig. 1. If we assume that \( \beta_1 \ll 1, \beta_0 \gg 1, \) and \( L_p > \alpha_1^{-1} > \alpha_0^{-1} \) then Eq. (22) reduces to

\[ PL \propto N(1-R) \frac{\alpha x_p}{\tau_r} e^{-(\alpha_0 + \alpha_1) w} \left( \frac{1}{\beta_0} + \frac{1}{b} \right) \left( 1 - e^{-ad} \right). \]  

(23)

A comparison of the PL intensity from a structure with two different surface depletion widths assuming \( \beta_0 \gg b \) or that \( \beta_0 \) does not change with a change in surface potential, results in

\[ \frac{PL_2}{PL_1} = \frac{1 - e^{-(\alpha_0 + \alpha_1) \Delta w}}{1 - e^{-(\alpha_0 + \alpha_1) \Delta w}}, \]  

(24)

or

\[ \frac{t_2}{t_1} = \frac{P}{P_1} e^{-(\alpha_0 + \alpha_1) \Delta w}, \]  

(25)
by C-V measurements. A semi-insulating (100) GaAs substrate is pictured in Fig. 3. Samples were grown with GaAs doping levels ranging from $5 \times 10^{15}$ to $5 \times 10^{17}$ cm$^{-3}$ as characterized by C-V measurements. A semi-insulating (100) GaAs substrate was used to minimize contributions to the PL from the substrate.

MOVPE growth was performed in a low pressure (78 Torr) horizontal reactor. GaAs substrates on a graphite sus-
FIG. 4. PL spectra from a sample with a 2-µm-thick $n$-GaAs layer doped $3 \times 10^{16}$ cm$^{-3}$ at two different times (as indicated in Fig. 4) under (a) 0.0% SO$_2$, (b) 0.6% SO$_2$ in flowing N$_2$.

Light emitted from the sample was focused into a 1 m monochromator through a 715 nm cutoff filter to eliminate the reflected laser light. The slits were opened to 3.0 mm for maximum signal and a diffraction grating blazed at 630 nm was used. The light intensity was measured with a liquid-nitrogen-cooled Ge detector with good radiant sensitivity from 800 to 1500 nm. The 500 Hz component of the signal was maximized from a lock-in amplifier and recorded on a personal computer.

RESULTS AND DISCUSSION

A PL spectrum over the range 800–900 nm was recorded under nitrogen flow to determine the peak emission wavelength. The maximum of this broad peak was consistently found at 872 nm, coincident with the room temperature band-gap energy of GaAs. A similar spectrum was recorded during flow with 0.6% SO$_2$. Figure 4 shows the PL spectra from a 2 µm GaAs layer doped $3 \times 10^{16}$ cm$^{-3}$ $n$-type both with and without SO$_2$ present. The same peak positions were observed with and without SO$_2$, indicating that the sample temperature did not vary significantly with SO$_2$ concentration. Previous experiments had shown the PL intensity and peak position to be highly sensitive to sample temperature.

The PL intensity at 872 nm was monitored as a function of time while SO$_2$ was periodically introduced into the nitrogen flow. Figure 5 shows a typical result of the variation of PL intensity with time. The times at which the two spectra in Fig. 4 were taken are also indicated in Fig. 5.

The intensity of PL in Fig. 5 varies considerably with time. Two important features of this variation are common for all the samples. First, the intensity of PL decays exponentially in about an hour after photowashing, independent of SO$_2$ concentration. This is probably due to a "repinnning" of the surface Fermi level corresponding to a degradation of the photowashed surface by oxidation. While no studies have been performed to indicate how much oxygen is required to repin the photowashed GaAs surface, the 99.99% N$_2$ used apparently contained enough residual oxygen and/or water to reoxidize the GaAs surface. The time constant of degradation is consistent with that reported elsewhere. Second, an enhancement of the PL intensity in the presence of SO$_2$ above that expected without SO$_2$ may be seen. The assumed baseline (expected PL intensity without SO$_2$) is shown in Fig. 5 as a dashed line. Upon initial introduction of SO$_2$, a large, rapid enhancement of the PL intensity above the baseline occurs, but decays to a small, steady enhancement. The PL drops back to the baseline when the SO$_2$ is removed. Subsequent reintroduction of SO$_2$ results only in the small, steady enhancement. Notice that 2% SO$_2$ results in only a slightly larger enhancement of the PL intensity than 0.6%, indicating that the sites for surface adsorption are nearly saturated at these concentrations. This enhancement of PL intensity above the baseline appears to be fairly reversible and reproducible, but was significantly reduced after several hours due to the degradation of the photowashed surface. In further discussion, the steady fractional increase in PL intensity above the baseline will be used as an indication of the sensitivity of the various sample structures to electrical changes at the surface due to chemisorption of SO$_2$.

The initial rapid rise and slow decline to a steady value of the PL intensity on the first introduction of SO$_2$ is probably due to irreversible reactions on the photowashed surface that change the surface charge density greatly during the intermediate steps but by a decreasing amount as the reaction proceeds to completion. The kinetic effects observed thereafter may be due to several factors. The rise and fall of PL with a change in SO$_2$ concentration was on the order of 5 min as may be seen in Fig. 5. The time response of the mass flow controllers was about 6 s, while the residence time in the chamber was only 3 s. The slow changes may be explained by slow adsorption/desorption kinetics of SO$_2$ onto the surface. Perhaps a more likely explanation is slow charge carrier transport through the thick surface oxide [reported to be up to 95 nm of Ga$_2$O$_3$ (Ref. 24) using this photowashing
procedure. The effect would then be a result of slow electronic surface states.

The relative magnitudes of the PL intensity at 872 nm observed for all the samples are plotted in Fig. 6. These values were taken as proportional to the signal from the lock-in amplifier divided by the laser power. The measurements were taken prior to addition of any SO_2, approximately 30 min after completing the photowashing procedure. The PL peak from the sample doped 5x10^{15} cm^{-3} was below the noise level of the detector and thus unable to be measured. The predicted trend of the PL intensity with doping density and thickness of the GaAs layer using the FEM model described earlier is also shown in Fig. 6. These values were calculated assuming that the Fermi level at the surface is pined at 0.8 eV above the valence band and are shown as lines. The data and predictions both show a monotonic increase in the PL intensity with increasing doping density, but the data appear to increase more gradually than the predictions. This may be due to the unpinning of the surface Fermi level by photowashing, which should increase the PL intensity from lightly doped samples more than from heavily doped samples. Also, nonradiative recombination, which was not considered in the predictions, should be greater at higher doping levels. The effect on PL intensity of etching the GaAs layer to a thickness of 1 um was small, as predicted by the model. While the model predicted a very slight decrease in PL intensity, we were unable to distinguish any change within the experimental error.

The enhancement of PL intensity upon SO_2 introduction is believed to be caused by a change in the density of charged surface states upon SO_2 adsorption to the GaAs surface as discussed previously, though a change in surface recombination velocity has also been proposed by Meyer.\(^1\) Burk et al.\(^4\) have shown that the PL intensity is not affected by changes in the surface velocity as long as the flux of photogenerated carriers from the charge-neutral region into the surface depletion region is large enough (see the assumptions of Eq. (24)). Until now, it has been difficult to determine when this condition is satisfied because this carrier flux is determined not only by surface conditions but by the bulk transport properties of the semiconductor material and the electric field in the depletion region. The FEM calculations performed in this work directly allow this effect to be considered. Figure 7 shows the calculated photogenerated hole distribution using a wide range of surface recombination velocities.\(^2\) While the distribution of excess carriers in the surface depletion region is vastly different for different surface velocities, it is nearly identical in the charge neutral region and, thus, the PL is negligibly different. Other similar calculations have shown that only for nearly flatband GaAs surfaces, does the surface velocity play an important role in determining the PL intensity. The chemisorption of SO_2 in these experiments most likely changes both the surface charge density and the recombination velocity at the GaAs surface. Our FEM numerical results, though, have shown that the PL intensity changes observed may be accounted for solely by the changing surface charge density.

The steady state enhancement of the PL intensity caused by introduction of 0.6% SO_2 into the ambient N_2 flow is plotted in Fig. 8 for samples of various thicknesses and doping densities (shown as large points). These values were calculated as the fractional difference in the PL signal with 0.6% SO_2 from the estimated baseline PL. The predictions of both the FEM model (small points) and the analytical model using Eqs. (24) and (12) (lines) indicate that the observed PL enhancement due to SO_2 adsorption may be explained by a reduction in the density of negative surface charges by 9x10^9 to 2x10^{10} cm^{-2}. The data and model predictions clearly indicate a trend of larger sensitivity to changes at the surface from lightly doped GaAs layers than from heavily doped material. The effect of reducing the GaAs layer thickness to 1 um was to increase the sensitivity very slightly. This small increase in sensitivity from the 1 um layer was also predicted by our models. The predicted difference

---

FIG. 6. Relative magnitude of PL intensity from GaAs layers with various doping densities and thicknesses approximately 30 min after photowashing. 2 um layers are indicated with triangles. Layers etched to 1 um are indicated by squares. The lines show the predictions of the FEM model assuming the surface is pinned at 0.8 eV above the valence band. The dotted line shows the noise level of the detector.

FIG. 7. The density of photogenerated holes under a flux of 10\(^{18}\) photons/(cm\(^2\)s) at 458 nm in the GaAs layer pictured in Fig. 1 as calculated by the FEM code assuming surface recombination velocities, s, of 100, 10\(^2\), and 10\(^3\) cm/s.
layers with various doping densities and thicknesses. Large points show experimentally determined changes due to 0.6% SO$_2$ added to the N$_2$ flow. Small points (FEM) and lines [Eq. (24)] show the results of model predictions for a reduction by 9 x 10$^{10}$ and 2 x 10$^{10}$ cm$^{-2}$ in the density of negative surface charge. 2 $\mu$m layers are indicated with triangles and solid lines. Layers etched to 1 $\mu$m are indicated by squares and dashed lines.

between 1 and 2 $\mu$m layers, as seen in Fig. 2, though, is within our experimental error. According to Eq. (24), a large increase in sensitivity may only be achieved by reducing the layer thickness to about the depletion width, so that $t_d \sim \Delta W$, which is typically on the order of 10–1000 Å. Attempts to use layers of 0.5 $\mu$m thicknesses were unsuccessful, since the PL intensity at room temperature fell below the noise level of the detector.

**CONCLUSIONS**

We have derived analytical and numerical models to predict the effects of various parameters on the intensity of PL from semiconductor layers of finite thickness. The analytical model can predict trends in the sensitivity of the $n-n$ heterostructures studied here quite well, but the assumptions break down when a significant fraction of the PL intensity comes from the space-charge regions of the layer. Also, the analytical model cannot directly consider the effects of changing surface recombination velocities. Our FEM numerical model relaxes some of the assumptions of the analytical model, allowing these effects to be considered. The results of this model can then be used to show when the assumptions of the analytical model should hold.

The data and predictions presented here clearly show the trends of PL intensity and its sensitivity to SO$_2$ adsorption with the doping density of the semiconductor surface layer. For future studies of adsorption to GaAs surfaces and the eventual development of optical semiconductor chemical sensors, it is desirable to measure a strong signal (low noise) and have a large sensitivity to electrical changes at the surface. There is a tradeoff in the effect of semiconductor doping density in this respect: The largest, most easily measurable PL signal comes from the heavily doped samples, while the largest sensitivity to changes at the surface occurs with the lightly doped samples.

By reducing the thickness of the surface GaAs layer, the sensitivity to changes at the surface from these structures may be increased. It is, though, impractical to use this fact to significantly improve the sensitivity of the structures studied here because the relative magnitude of the PL intensity drops drastically at the thicknesses required. Other novel structures that may take advantage of thickness effects are presently under investigation.

Adsortion isotherms, such as those in Refs. 5 and 6, may, in theory, be constructed to calculate adsorption equilibrium constants, but present signal-to-noise ratios of our measurements do not allow accurate measurements at low concentrations. Continued efforts to raise signal-to-noise ratios using novel structures will allow such measurements and calculations to be made.

The instability of the photowashing surface preparation, as exhibited by the exponential decay of the baseline PL and reduced sensitivity after several hours, presented serious difficulties in this study. Future studies will greatly benefit from a surface preparation that results in a more stable unpinned surface. Alternative surface preparations are also currently under investigation.

**ACKNOWLEDGMENT**

This project was funded by the National Science Foundation (No. CTS-9202699).

---

10. C. Wilmsen, P. Kirchner, and J. Woodall, J. Appl. Phys. 64, 3287 (1988).