

Effects of passivating ionic films on the photoluminescence properties of GaAs

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The passivating effects of spin-coated films of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ on GaAs surfaces have been studied using room-temperature photoluminescence (PL) and low-temperature PL spectroscopy. After passivation, the 300 K PL efficiency is increased on both *n*- and *p*-type material; improvements of up to $2800\times$ are observed. The surface field and surface recombination-related notch features in the free and bound exciton emission spectra at low temperature are eliminated, implying that the residual band bending under illumination is less than 0.15 V.

Oxygen-exposed GaAs surfaces possess a large density of extrinsic states near the middle of the forbidden energy gap, which effectively pin the surface Fermi level at that position.^{1,2} These pinning states have hindered the development of a successful GaAs metal-insulator-semiconductor technology.³ Moreover, the midgap pinning of the Fermi level greatly increases the nonradiative recombination rate at surface recombination centers.⁴ The latter effect is responsible for the “ $2kT$ ” current⁵ which limits the performance of minority-carrier devices such as light-emitting diodes, lasers, solar cells, and bipolar transistors.

Chemical⁶ or photochemical⁷ treatments to passivate GaAs surfaces are consequently of great interest. Recently, a novel technique involving spin-coated films of wide band-gap inorganic sulfides was reported.^{8,9} These films produced 60-fold improvements in the gain of heterojunction bipolar transistors at low current levels,⁸ and reduced surface recombination velocities to values as low as 500 cm/s.⁹ In this letter, we use photoluminescence (PL), one of the most sensitive and widely employed methods of characterizing non-radiative surface recombination,^{5-7,10} to study these surfaces.¹¹

The samples consist of various (100) oriented structures (described below in detail) grown by molecular beam epitaxy (MBE), organometallic chemical vapor deposition (OMCVD), and vapor phase epitaxy (VPE). Details of the passivation procedure are described elsewhere.⁸ Briefly, the sample is first lightly etched in a (1:8:500) solution of ($\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$) to obtain a hydrophilic surface, then rinsed and spun dry. A few drops of ~ 1.0 M aqueous solution of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ are applied to the surface and the sample is spun in air at about 5000 rpm until dry. Room-temperature PL measurements are performed with the sample in a sealed, He-filled chamber. Low-temperature measurements are performed with the sample freely suspended in a superfluid He bath at 1.8 K. The excitation is provided by an Ar^+ ion laser operating at 5145 Å. A fixed excitation level of ~ 10 W/cm² is employed at 300 K, while the 1.8 K spectra shown here were recorded at ~ 700 mW/cm². A 1.0-m double spectrometer, a GaAs photomultiplier tube, and a photon counting detection system are used. The data have been corrected when necessary for the spectral response of the system. Intensity measurements are generally reproducible to within $\pm 30\%$ or better.

The strength of the room-temperature PL signal is

shown in the upper two curves in Fig. 1 for two *n*-type GaAs samples as a function of surface treatment. As the spectral shape of the luminescence is typical of band-to-band transitions and does not change, we indicate only relative intensities. Application of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ yields improvements of up to $2800\times$ in the PL intensity with respect to that of a freshly etched surface for the low-doped sample, restoring to within 15% the intensity obtained with the original AlGaAs clad-

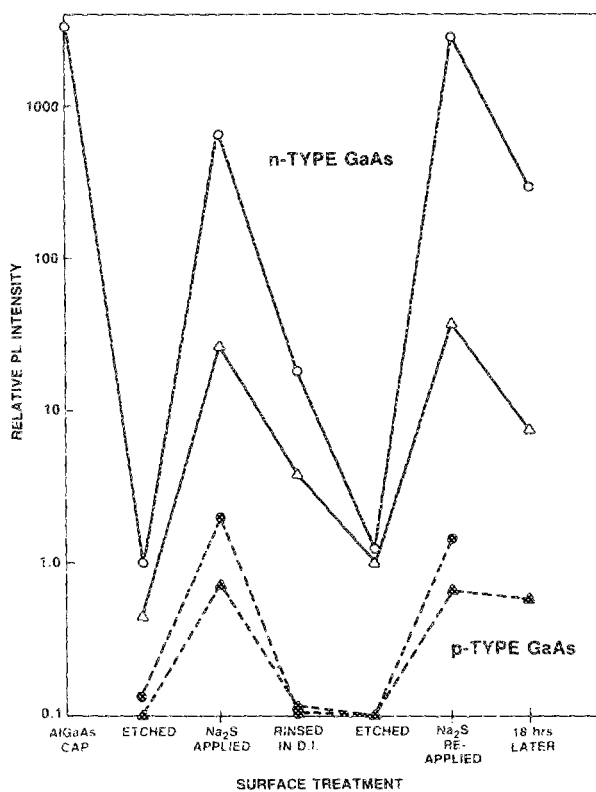


FIG. 1. Relative PL intensities at 300 K for four GaAs samples as a function of surface treatment. (Open circles) OMCVD GaAs layer, $7.0\ \mu\text{m}$ thick, $n = 6 \times 10^{13}\ \text{cm}^{-3}$, sandwiched between two $0.1\text{-}\mu\text{m}$ -thick $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ layers; the top AlGaAs layer is removed in the first etching step. (Open triangles) OMCVD GaAs layer, $0.31\ \mu\text{m}$ thick, $n = 9 \times 10^{16}\ \text{cm}^{-3}$, grown on a $0.55\text{-}\mu\text{m}$ -thick $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ buffer layer. (Closed circles) a $9.1\text{-}\mu\text{m}$ -thick layer, $p = 4 \times 10^{15}\ \text{cm}^{-3}$, grown on a semi-insulating (SI) GaAs substrate. Initial “etched” state corresponds to Na_2S rinsed off (no chemical etch). (Closed triangles) a $3.2\text{-}\mu\text{m}$ -thick layer, $p = 1 \times 10^{18}\ \text{cm}^{-3}$, grown on a SI substrate. Initial “etched” state actually air exposed. Intensities are normalized to the etched condition for each sample; lower two curves are displaced down one decade for clarity.

ding layer. Improvements for the more heavily doped sample are smaller, primarily because this layer is thinner, which results in larger residual surface recombination after treatment. (The quantum efficiencies of the two samples are about the same before treatment.) Variations between successive $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ applications are believed to result from changes in the wetting properties of the surface and resultant film quality.

Residual improvements in PL efficiency are observed even after thoroughly rinsing off the bulk of the film in de-ionized water, presumably due to the presence of a passivating submonolayer surface phase.^{8,9} The data indicate a degradation in the properties of the hygroscopic $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ films when exposed overnight to humid air; under drier conditions we found essentially no change on this time scale.

Similar, though less pronounced improvements are observed on *p*-type samples of low and high doping levels, as shown in the lower two curves in Fig. 1. The maximum improvement obtainable in these samples is smaller, due in large part to the absence of underlying AlGaAs buffer layers and the consequent diffusion of carriers into the highly non-radiative substrates.

The improvements we observed after $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ passivation in the PL efficiency of both heavily doped *p*- and *n*-type material in the low injection regime are consistent with a reduction in surface recombination center density and/or unpinning of the surface Fermi level by the treatment. However, these observations alone do not rule out the alternative explanation that we have merely repinned the Fermi level closer to one of the band edges. Assuming low level injection and quasi-equilibrium between the surface and the electrically neutral bulk, the surface recombination velocity *S* resulting from recombination through a given trap is given by⁴

$$S = (n_0 + p_0) / [S_{p0}^{-1}(n_s + n^*) + S_{n0}^{-1}(p_s + p^*)].$$

Here, S_{p0} and S_{n0} are proportional to the concentration and capture cross sections of the trap, n_0 and p_0 are the equilibrium bulk electron and hole densities, n_s and p_s are the electron and hole densities at the surface *under illumination*, and n^* and p^* are the densities which would be present if the Fermi level were coincident with the trap level. Bare GaAs surfaces exhibit large values of *S* primarily because the Fermi level is pinned near midgap, so that $n_s + p_s$ is minimized (note that $n_s p_s$ is constant).⁴ If a given surface treatment pins the Fermi level near one of the band edges, then either n_s or p_s will be large, regardless of the bulk doping, and *S* will be reduced on both *n*- and *p*-type material. An additional measurement, such as the capacitance-voltage data presented by Offsey *et al.*,⁷ is necessary to eliminate this possibility. In the following, we demonstrate that the low-temperature PL spectra provide the needed evidence.

A low-temperature excitonic luminescence spectrum from a VPE GaAs sample is shown in Fig. 2 both before and after passivation by $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. The spectrum of the untreated sample is typical of high-purity GaAs.¹² In particular, notch or dip features are observed at the locations expected for both ground-state neutral donor-bound exciton (D^0, X) and longitudinal free-exciton (FE) luminescence. The notch in the (D^0, X) peak is usually observed in *n*-type

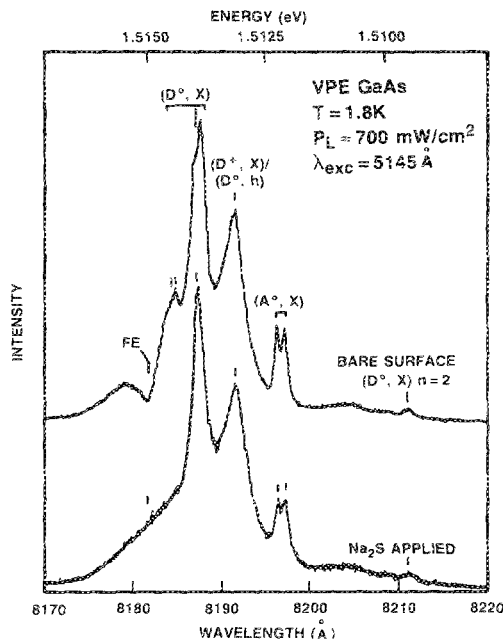


FIG. 2. Normalized excitonic luminescence spectra (intensity in arbitrary units) of an *n*-type VPE GaAs layer ($n = 4 \times 10^{14} \text{ cm}^{-3}$, 77 K mobility = $92\,000 \text{ cm}^2/\text{V s}$) before and after $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ surface passivation. The position of the ground state (D^0, X) peak is indicated by the tic mark at 8187 \AA . Two excited states are also marked at shorter wavelengths. Incident laser intensity (P_L) and wavelength (λ_{exc}) are indicated.

material at a sufficiently high excitation intensity, and is ascribed to self-absorption in a region near the surface where the density of the (D^0, X) complexes is reduced by surface recombination.^{12,13}

The notch in the free exciton/polariton peak has been ascribed both to enhanced trapping of polaritons near the surface¹⁴⁻¹⁶ (i.e., nonradiative surface recombination) and to self-absorption in a portion of the space-charge layer at the surface where the polaritonic resonance is modified by the electric field.¹⁷ Irrespective of the chosen model, the presence of surface charge and/or surface recombination centers is known to be essential in producing the notch, since surfaces cleaved in vacuum do not display the notch until they are exposed to oxygen¹⁸ and samples clad with an AlGaAs cap layer do not display the notch until the cap layer is removed.¹⁷

After the $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ coating is applied, both notches are eliminated. A small amount of inhomogeneous strain, resulting from differential thermal contraction of the GaAs and the Na_2S film, is believed to be responsible for the slight broadening of the (A^0, X) doublet and the (D^0, X) excited states; the latter peaks are no longer resolved. The absolute PL intensity is *reduced* by a factor of about 3.5, which we tentatively attribute to scattering by the polycrystalline surface film. The absence of *improvements* in the PL efficiency suggests that recombination associated with the bare surface does not limit the lifetime at low temperature as it does at 300 K.

Similar data are presented in Fig. 3 for a *p*-type MBE sample. The spectrum of the sample before passivation is dominated by (A^0, X) and "defect" acceptor-bound exciton (d, X) features; a strong notch is present in the center of the

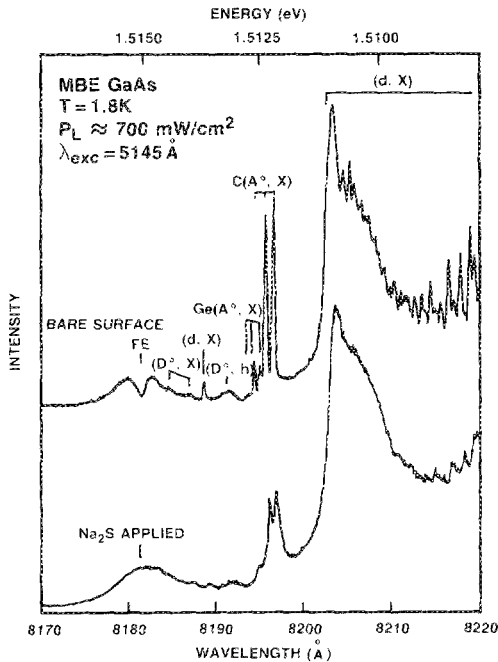


FIG. 3. As Fig. 2, but for a p -type MBE GaAs sample ($\rho = 4 \times 10^{15} \text{ cm}^{-3}$), before and after $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ surface passivation.

FE peak. After application of a $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ film, the (A^0, X) and (d, X) peaks are broadened by the strain effect mentioned above. More important, the FE line shape no longer displays any notch.

The presence of the FE notch in the PL spectrum of this untreated p -type sample has some interesting implications for the mechanism by which such notches are produced. In particular, Lee *et al.* and Steiner *et al.* have argued that neutral donor concentration is an important factor in producing the notch.^{15,16} The proposed mechanism involves elastic scattering of the polariton modes in the vicinity of the longitudinal exciton energy by neutral donors, which in conjunction with the small group velocity of these modes slows the diffusive transport of polaritons from the bulk to the surface and thereby enhances the effects of inelastic scattering and surface trapping.

In the p -type sample of Fig. 3, the neutral donor concentration is essentially negligible, since the (D^0, X) peak is virtually absent. Therefore, the notch in the FE peak in this sample cannot be attributed to the effects of polariton scattering by neutral donors. Elastic scattering of polaritons by neutral acceptors might be considered in this case, but the calculations of Lee *et al.*¹⁵ conclude that acceptor scattering is much less effective than donor scattering, and will produce only an asymmetric single peak rather than a notched "double" peak.

The presence of notches in our moderately doped n - and p -type material and their absence in some high-resistivity p -type samples studied by Lee *et al.*¹⁵ is consistent with the

role of residual surface fields on the spectral transmissivity of the surface for polaritons, as emphasized in the theory of Schultheis and Tu.¹⁷ Surface fields are expected for moderate illumination if the equilibrium bulk Fermi level is close to either band edge (since the surface Fermi level is pinned midgap¹), but not in high-resistivity samples where the bulk Fermi level is near midgap. Direct measurements of the surface field under illumination would be highly desirable to test this model.

The elimination of the surface-related notches in the spectra of both n - and p -type material rules out the possibility that the surface treatment has repinned the Fermi level near one of the band edges. In that case, a large electric field would exist at the surface under moderate illumination on either the n - or the p -type material, which is known to produce a notch in the FE peak.¹⁷ An upper limit on the residual band bending in the illuminated n -type sample at low temperature is estimated to be about 0.15 V, based on a comparison with the data of Ref. 17. We therefore conclude that the $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ treatment substantially reduces the density of pinning and/or recombination centers on oxygen-exposed GaAs surfaces.

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