A near-field scanning optical microscopy study of the uniformity of GaAs surface passivation

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We have achieved spatially resolved photoluminescence (PL) from metalorganic vapor phase epitaxy (MOVPE) grown GaAs surfaces by near-field scanning optical microscopy (NSOM). We have performed the topography, reflection, and PL measurements by NSOM combined with the topography measurements by atomic force microscopy (AFM) on the as-grown and $(\text{NH}_4)_2\text{S}$ -passivated GaAs samples. The uniformity of GaAs with a thin $\text{Al}_{0.65}\text{Ga}_{0.35}\text{As}$ cap layer has also been studied and compared with the $(\text{NH}_4)_2\text{S}$ treated samples. We found the submicron scale variations in PL intensity which were not correlated to the topographic features. The PL intensity variation was related to the changes in the surface state density. Semiquantitative analyses of the resolution limits of NSOM-based PL measurements and surface state variations are presented.

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Most as-grown III–V semiconductor surfaces possess a very high surface state density ($N_s \sim 10^{12} \text{ cm}^{-2}$), particularly after exposure to air.¹ These surface states are nonradiative recombination centers which impact the performance of many minority carrier devices, such as light emitting diodes, solar cells, heterojunction bipolar transistors, and lasers. This high density of surface states leads to Fermi level pinning near-midgap, resulting in difficulties in the Ohmic contact formation and in the fabrication of metal-insulator-semiconductor field-effect transistors (MISFET).² In recent years, many studies have focused on the effective passivation of the compound semiconductor surfaces.³ $(\text{NH}_4)_2\text{S}$ passivation of GaAs surfaces has been proven to be very successful and easy to implement.⁴

Several characterization techniques have been used to probe the properties of the passivated surfaces.^{5,6} The uniformity of passivation at submicron scale, however, has rarely been studied. As the device dimensions decrease to the nanoscale, the surface properties and uniformity of these properties at the submicron scale become increasingly important.⁷ Near-field scanning optical microscopy (NSOM) has been demonstrated to be a powerful tool for performing optical measurements at a much higher spatial resolution than conventional far-field optics.⁸ In this work, the spatially resolved PL measurements on the passivated GaAs surfaces, using NSOM, are presented. These quantitative measurements provide information on the surface state density variation as well as the independently determined surface morphologies of the passivated surface. Measurements of the optical uniformity of $(\text{NH}_4)_2\text{S}$ -passivated surfaces are compared to control samples consisting of a thin $\text{Al}_{0.65}\text{Ga}_{0.35}\text{As}$ cap layer on an epitaxial GaAs layer. This structure serves as an alternative GaAs surface passivation. The epitaxially grown $\text{GaAs-Al}_x\text{Ga}_{1-x}\text{As}$ heterostructure has a low interface state density and interface recombination velocity^{9,10} and should have more uniform properties than the free GaAs surface.

The NSOM is a home-built system with a commercial scanning control unit.¹¹ All the experiments are done in illumination mode where the NSOM tip serves as the excitation

source. The optical collector is a parabolic reflector with the tip at its focal point, maximizing the collection efficiency. A low level He–Ne laser light is used for the standard shear force distance regulation.¹² Topographic and optical images are collected simultaneously with the detection wavelength fixed at the band-edge energy of GaAs (870 nm).

All the samples used in this study were grown by metalorganic vapor phase epitaxy (MOVPE) on GaAs (001) wafers misoriented by 2° towards the nearest $\langle 110 \rangle$ azimuth. The GaAs epitaxial layer was 1 μm thick with p -type Zn doping of $9 \times 10^{19} \text{ cm}^{-3}$. The passivation process consisted of the removal of native oxides by soaking the sample in hot $\text{H}_2\text{SO}_4:\text{H}_2\text{O}(1:1)$ solution, followed by a shallow 30 nm etching of GaAs in a dilute solution of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}(1:8:500)$, a DI water rinse for 5 min, treatment in a 22% solution of $(\text{NH}_4)_2\text{S}$ in H_2O for 5 min and a final DI water rinse for 5 min.² A control sample consisted of similarly doped epitaxial p -GaAs with a 3 nm thick p -type $\text{Al}_{0.65}\text{Ga}_{0.35}\text{As}$ cap layer. This sample was used in the “as-grown” condition.

We obtained surface scans of the topographic, reflection and PL signals on the as-grown, passivated and $\text{GaAs-Al}_{0.65}\text{Ga}_{0.35}\text{As}$ heterostructure samples. Figure 1 shows the simultaneously collected topography and reflection images from a GaAs sample after $(\text{NH}_4)_2\text{S}$ surface passivation. The NSOM topography features at submicron scale are very similar to those observed by atomic force microscopy (AFM). Similar values of the rms roughness were obtained by NSOM and AFM on all samples, indicating both a stable NSOM distance regulation and a high sensitivity to subnanometer height variation. The PL image, shown in Fig. 2, indicates luminescence variations on the submicron spatial scale that are clearly observed. The surface optical and topographic structures were analyzed through the determination of the lateral correlation functions and are presented in the figure captions. The lateral correlation lengths were determined which represent the smallest feature sizes within resolution limits of the instrument for the topographic and optical signals.¹³ These values indicate we have achieved submicron spatial resolution for the NSOM-based optical and topo-

FIG. 1. Simultaneously collected $2.6 \mu\text{m} \times 2.6 \mu\text{m}$ (a) reflection and (b) topography signals from a GaAs sample after $(\text{NH}_4)_2\text{S}$ surface passivation. A strong coupling between the reflection and topography signals is observed. The lateral correlation lengths for the two images are 75 and 39 nm, respectively. The cross correlation coefficient for the two images is 0.59.

FIG. 2. Simultaneously collected $2.4 \mu\text{m} \times 2.4 \mu\text{m}$ PL (a) and topographic (b) signals from an as-grown GaAs surface. Negligible coupling exists between the topography and PL signals. A tip with a larger aperture was used in this scan. The lateral correlation lengths for the two images are 116 and 120 nm, respectively. The cross correlation coefficient for the two images is -0.04 .

TABLE I. Analysis of spatially resolved PL measurements using NSOM.

	$\Delta\text{PL} \pm \sigma_{\Delta\text{PL}}$	$\Delta N_s \pm \sigma_{\Delta N_s}$	NSOM topography $\text{rms} \pm \sigma$ (nm)	AFM $\text{rms} \pm \sigma$ (nm)
As-grown	0.86 ± 0.05	0.42 ± 0.02	0.25 ± 0.03	0.23 ± 0.01
$(\text{NH}_4)_2\text{S}$ passivated	0.73 ± 0.02	0.35 ± 0.01	0.24 ± 0.01	0.27 ± 0.06
$\text{Al}_{0.65}\text{Ga}_{0.35}\text{As}$ capped	0.59 ± 0.06	0.28 ± 0.03	0.38 ± 0.08	0.31 ± 0.02

graphic measurements. The quantitative cross-correlation coefficient analysis,¹⁴ carried out on a pixel-by-pixel basis, indicates a negligible correlation between the topography and PL signals in contrast to the strong correlation between the measured topography and reflection signals.¹⁵

A theoretical model was developed in order to relate the PL intensity variation to the change of surface state density and to estimate the spatial resolution limit. The specific surface state density and bulk doping distribution determine the band bending and the electric field within the depletion region. Assuming a typical minority carrier lifetime in the bulk of 0.1 ns, we used the one-dimensional analytic solution of Mettler¹⁶ to calculate the functional dependence of the PL intensity on surface state density. Within this model, Mettler characterized minority carrier transport to the surface through the use of a virtual recombination velocity, S_v , at the depletion region boundary:

$$\text{PL} \propto (1-R)N e^{-(\alpha_e + \alpha_p)w} \frac{\alpha_e L_n}{(\alpha_e L_n)^2 - 1} \times \left(\frac{S_v L_n / D_n + \alpha_e L_n}{(S_v L_n / D_n + 1)(\alpha_p L_n + 1)} - \frac{1}{(\alpha_e + \alpha_p) L_n} \right), \quad (1)$$

where R is the surface reflectivity, N is the excitation intensity, α_e and α_p are the absorption coefficients at the excitation and emission wavelengths, L_n and D_n are the diffusion length and diffusion coefficient of the minority carriers. For the highly doped samples in this study, the depletion region is so narrow, smaller than 3 nm, that the PL from the depletion region is estimated to be less than 10^{-6} of the total PL. Therefore, the virtual recombination velocity, S_v , in this limit, becomes the actual surface recombination velocity S . Under low illumination conditions, the recombination velocity has the form, $S = N_s \sigma v_{th}$, where N_s is the surface state density, σ is the capture cross section and v_{th} is the thermal velocity of carriers. We measure the variation in the $N_s \sigma$ product, since v_{th} is a constant. Because the nature of the surface states is assumed not to change with passivation, we will assume the variation in PL is due directly to the local variation in N_s , i.e., σ is a constant.

This model was used to analyze the data derived from the NSOM with results shown in Table I, where ΔPL is defined as the percentage rms variation of the PL signals. The percentage variation of surface (interface) state density ΔN_s is calculated from ΔPL using Eq. (1). The associated error in these values is also presented in this table. The analysis shows that the surface (interface) state density variation is on the order of several percent over a $2.38 \mu\text{m}$ region

FIG. 3. The results of the numerical modeling of the localized PL obtained from *p*-type GaAs using NSOM. (a) The calculated photogenerated carrier distribution in a cross section perpendicular to the surface has a lateral decay length (~ 55 nm) which is much smaller than the intrinsic diffusion length as a result of the carrier recombination at the surface. (b) The lateral plot of the carrier flux to the surface indicates a rapid drop off with an e^{-1} width of ~ 120 nm.

for all the samples. The comparison between the state density variation for the three materials is: $\text{Al}_{0.65}\text{Ga}_{0.35}\text{As-capped} < (\text{NH}_4)_2\text{S-passivated} < \text{As-grown}$. In addition to possessing the observed strongest PL intensity level, the $\text{Al}_{0.65}\text{Ga}_{0.35}\text{As-capped}$ sample exhibited the lowest variation in interface state density. It is expected that since the interface was produced through the epitaxial growth process, it should be more uniform than the free surface or a surface passivated by wet chemical treatment.^{9,10}

As in all scanning probe measurements, the spatial resolution of the measured signal is of great interest. The spatial resolution limit of the localized PL experiments using NSOM can be estimated from an analytic calculation of the carrier transport and recombination in lateral directions. We ignore the depletion region and assume a point excitation source near the surface. The two-dimensional carrier transport equation was solved assuming that the surface has an

infinite surface recombination velocity and recombination in the bulk is characterized by a single recombination lifetime. As shown in Fig. 3, the presence of surface states greatly narrows the lateral distribution of the photogenerated carriers, leading to the lateral resolution limit of about 120 nm. Since the aperture size of the NSOM probe we used is less than 90 nm,¹¹ the spatial resolution should be minority carrier diffusion limited. The lateral correlation length obtained from the PL image (Fig. 2) is 116 nm, indicating it is associated with the spatial resolution of the localized PL measurements using NSOM. This calculation also indicates that the recombination rate at the surface is not saturated, even at the high excitation density used in these NSOM experiments, provided the surface recombination time constant is less than 100 ns. Given the negligible depletion width in these measurements, the observed variation in the optical signal should therefore be directly related to the surface state density.

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