

Correlation between Photoluminescence and Surface State Density on GaAs Surfaces Subjected to Various Surface Treatments

Hideki Hasegawa, Toshiya Saitoh, Seiichi Konishi,

Hirotatsu Ishii and Hideo Ohno

Department of Electrical Engineering, Faculty of Engineering
Hokkaido University, Sapporo, 060 Japan

Relationship between the band edge PL intensity and surface state density was investigated theoretically and experimentally for GaAs surfaces subjected to various surface treatments.

It is shown that increase of PL intensity does not necessarily correspond to reduction of surface state density. A new mechanism based on fixed charge generation and not on N_{ss} reduction is proposed for PL enhancement by photochemical oxidation and by Na_2S deposition. Marked N_{ss} reduction by HCl treatment is also reported.

1. INTRODUCTION

It is generally accepted that photoluminescence (PL) is a surface sensitive technique and that higher band edge PL intensity implies better surface quality with reduced of surface state density. Such a simple correlation is, however, not well founded either theoretically or experimentally.

The purpose of the present paper is to investigate both theoretically and experimentally the relationship between the band edge PL intensity and the surface state properties in the case of GaAs surfaces subjected to various surface treatments.

A rigorous theoretical analysis of surface recombination and PL intensity was made on computer for various possible types of surface state distributions. Then, the result was applied to the interpretation of the experimentally observed change of PL intensity on (100) GaAs surfaces before and after several surface treatments. The treatments investigated include the two recently found surface treatment techniques for GaAs, i.e., photochemical oxidation in water¹⁾ and depo-

sition of Na_2S ²⁾ as well as and exposure to HCl and NH_3 gas ambients. In order to get information on surface state distributions and the position of surface Fermi level in the dark, the change of the surface band bending was also measured by XPS and surface current transport (SCT) techniques.

2. APPROACH FOR PL INTENSITY CALCULATION

Relative intensity of band edge intensity was evaluated by calculating the excess pn product under photoexcitation and integrating it from surface into bulk. The surface recombination process was described by the following Shockley-Read-Hall (SRH) expression for recombination rate U_s .

$$U_s = \int_{E_v}^{E_c} \frac{\sigma_n \sigma_p v_{th} (pn - n_i^2) N_{ss}(E)}{\sigma_n (n + n_1) + \sigma_p (p + p_1)} dE \quad (1)$$

where conventional notations are used. Surface states controls not only the recombination process but also the band bending through its charge. Thus, overall self consistency is required among re-

combination, generation, carrier flow and charge neutrality, band bending, occupation status of surface states and positions of quasi Fermi levels of carriers.

To solve the above extremely complicated problem, a computer program was developed in which the microscopic current equation, Poisson's equation, SRH statistics and overall charge neutrality condition were applied to the interface region. These equations were expressed in vector-matrix forms and self-consistent solutions were obtained by a standard iterative procedure after Scharfetter and Gummel³⁾.

For the distribution of surface state density (N_{ss}), discrete type of distributions with Gaussian profiles and U-shaped continuum type of distributions with arbitrary U-shape curvature and minimum density N_{ss0} were investigated. According to our DIGS (disorder induced gap state) model⁴⁾, N_{ss} distribution in compound semiconductor-insulator interfaces is given in general by the latter type of distributions with a characteristic charge neutrality energy level E_{H0} giving the minimum density.

Possible presence of fixed surface charge Q_{fc} was also taken into consideration in the program.

3. EXPERIMENTAL

Band edge PL intensity was measured on (100) GaAs surfaces after initial wet chemical etching by ammonia based solutions ($NH_4OH:H_2O_2:H_2O=1:1:50$) and subsequently after various surface treatments including photochemical oxidation in water, and exposure to gas ambients of NH_3 and HCl with or without UV light irradiation (ArF excimer laser, 193nm). Excitation was done by Ar laser light (5145 nm) at a incident photon flux density of about 10^{17} - 10^{18} $cm^{-2}s^{-1}$, and the band edge luminescence at 867 nm was synchronously detected at room temperature.

Setup for photochemical oxidation was similar to that by Offsey et al¹⁾, and described in ref.5 together with oxidation data. Na_2S film was formed by spun-on deposition at 3000 rpm. Exposure to NH_3 and to HCl was done both in atmosphere and in UHV-tight chamber.

Change of surface band bending in the dark caused by surface treatments was also detected by measurements of XPS core level shifts and surface current transport (SCT). The latter utilizes an ungated FET structure shown in Fig.1, and detects directly the shift of the surface Fermi level.

4.RESULTS AND DISCUSSION

4.1 Chemically Etched Surface

The theoretical analysis indicated that PL intensity varies in a complex manner with the distribution shape and density of surface states, energy location of density minimum, sign and amount of fixed surface charge and the excitation wavelength and intensity. In most cases, reduction of surface state density increases PL intensity but increase of PL intensity does not necessarily correspond to reduction of surface states. In the extreme cases where surface states tend to pin the Fermi level near band edges, PL intensity increases with the increase of N_{ss} .

In order to deduce the N_{ss} distribution on the chemically etched GaAs surfaces, band

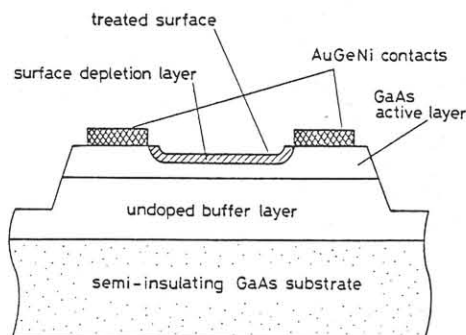


Fig.1 Ungated FET structure for SCT measurement. Fermi level shift is directly detected.

bending was studied for n- and p-materials with different doping by XPS technique. Then, using the DIGS model with $E_{H0} = 0.475 \text{ eV} + E_V$ for GaAs⁴⁾, the observed data was fitted to deduce N_{SS} distribution on the assumption that the observed band bending is determined by the charge balance between the bulk and the DIGS continuum. The result is shown in Fig.2.

The calculated excitation wavelength dependence of PL intensity using the distribution in Fig.2 is shown in Fig. 3 together with the experimental result after Mettler⁶⁾. Excellent agreement between theory and experiment is seen in Fig.3. Such agreement could not be obtained for discrete type of N_{SS} distributions.

4.2 Effects of Surface Treatments

The experimentally observed effects of various surface treatments on PL intensity and on band bending in the dark are summarized in Table 1. Both of photochemical oxidation in water and Na_2S deposition led to marked increase of PL intensity as previously reported^{1,2)}, but with simultaneous increase of band bending in the dark for n-type materials. On the other hand, marked

increase of PL intensity with simultaneous reduction of band bending was observed for n- and p- type materials after exposure to HCl . Exposure to NH_3 resulted in small reduction of band bending with no appreciable change in PL intensity .

Table 1 Effects of various surface treatments on PL intensity and band bending in dark

	type	PL intensity	Fermi level shift E_{Fs}
photochemical oxidation	n	12	-0.4~-0.6
	p	6	-0.03
Na_2S deposition	n	5	-0.3~-0.6
	p	9	-0.08
exposure to HCl in air (light)	n	17	+0.3
	p	5.5	-0.02
exposure to HCl in UHV chamber	n	-	+0.2
exposure to NH_3 air(light)	n	-	+0.03
exposure to NH_3 in UHV chamber	n	0.9	+0.05~+0.1

* $n : N_D = 1 \times 10^{16} \text{ cm}^{-3}$, $p : N_A = 1 \times 10^{17} \text{ cm}^{-3}$
 ** PL intensity is given in relative to chemically etched surface
 *** E_F at chemically etched surfaces
 $n : E_C - 0.70 \text{ eV}$, $p : E_V + 0.40 \text{ eV}$
 negative sign means downward shift and positive upward

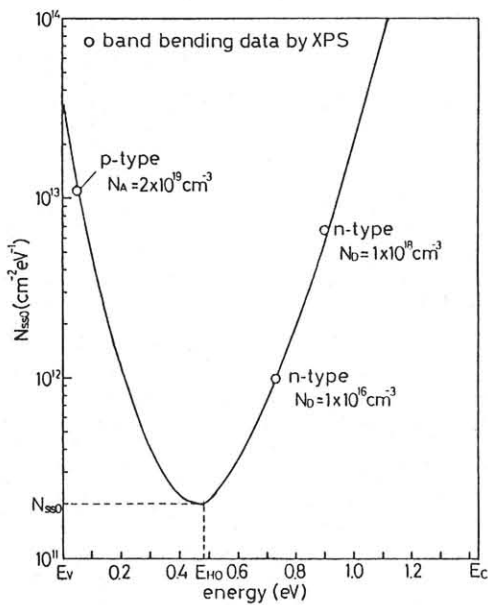


Fig.2 N_{SS} distribution on the chemically etched GaAs deduced from XPS measurement.

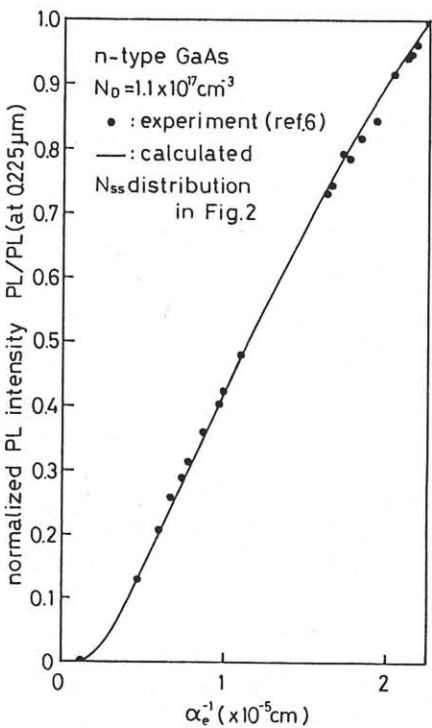


Fig.3 Calculated and measured PL intensity vs. excitation wavelength

4.3 Discussion

Normalized PL intensity calculated changing the surface state density is shown in Fig.4. The distribution shape was kept the same with that in Fig.3 and the minimum density value N_{ss0} was varied. PL intensity is normalized by that for the N_{ss} distribution in Fig.2. As seen in Fig.4, PL intensity is increased and the band bending is reduced as N_{ss0} is reduced.

On the other hand, the observed behavior of PL intensity and shift of Fermi level in the dark is far more complex as see in Table 1. After many trials, it was found that contradictory movement of PL intensity and band bending after photochemical oxidation and Na_2S deposition can only be reconciled by having a certain mechanism of pulling the Fermi level down near to VBM. A simplest and most likely mechanism of such is generation of negative fixed charge. The calculated PL intensity for such case is shown in Fig.5 where the effect of fixed charge is expressed modified charge neutrality point E_N of total surface charge. The result in Fig.5 is in quantitative agreement with the result in Table 1.

In contrast to this, behavior after exposure to HCl can only be explained by substantial reduction of surface state density.

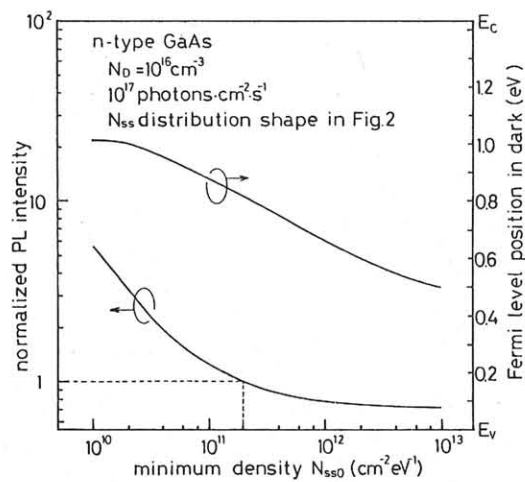


Fig.4 Calculated PL intensity and band bending in dark vs. surface state density

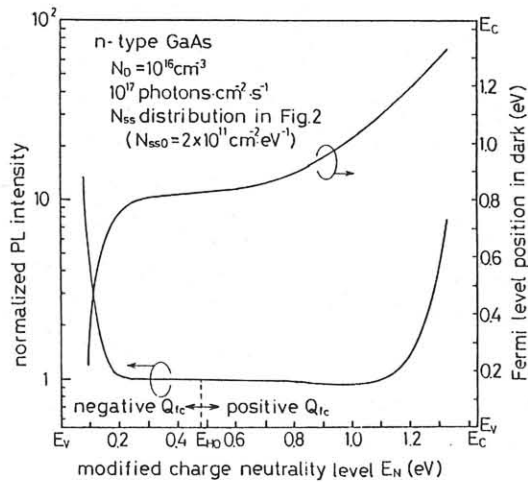


Fig.5 Calculated PL intensity and band bending in dark vs. modified charge neutrality energy E_N due to fixed charge.

5. CONCLUSION

The hitherto unsolved issue concerning the relationship between PL intensity and surface states is rigorously addressed theoretically and experimentally. Danger in assessing surface quality by PL intensity only is pointed out. A new PL enhancement mechanism based on fixed charge generation and not on N_{ss} reduction is proposed for photochemical oxidation and Na_2S deposition. Marked N_{ss} reduction by HCl treatment is reported for the first time.

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