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In-Situ Surface State Spectroscopy by Photoluminescence and Surface Current Transport for Compound Semiconductors

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By a rigorous computer analysis, it is shown that the surface state distributions on semiconductor free surfaces can be determined by detailed measurements of the band-edge photoluminescence (PL) efficiency as a function of the excitation intensity. The measurement of the Fermi level pinning position in the dark by the surface current transport measurement avoids the ambiguity of the interpretation.

The new technique is successfully applied to variously treated GaAs surfaces and to passivated InGaAs surfaces with and without the ultrathin Si interface control layer.

1. INTRODUCTION

Except for the STM technique for clean surface, there exists no known way to measure the density distributions of surface states on technological important "free" surfaces of semiconductors such as epitaxially grown clean surfaces, air-exposed or intentionally lightly oxidized wet or dry etched surfaces and surfaces exposed to various gas ambients or subjected to various chemical treatments like the sulfur treatment.

The purpose of this paper is to show, for the first time, that an in-situ determination of the surface state density (N_{ss}) distribution on free surfaces is possible by the measurements of the band edge photoluminescence (PL) under photo-excitation combined with the surface current transport measurement in the dark.

2. PRINCIPLE OF NOVEL SURFACE STATE SPECTROSCOPY

Previous analysis of $PL^{1,2}$ assumed that the so-called surface recombination velocity S is a constant. However, we have shown³) recently that S is not a constant but depends, for a given distribution of surface states, strongly on the light spectrum and intensity, conduction type and doping of semiconductor etc.

The dependence of S_e on the excitation intensity, ϕ , is schematically shown in Fig.l(a). The reduction of S_e with the increase of ϕ is caused largely photo-induced flattening of the band.

The corresponding behavior of the band-edge



Fig.l Behavior of S_e and PL efficiency spectra.

PL intensity, I_{PL} , is schematically shown in Fig.1(b). The PL behavior in Fig.1(b) consists of three distinct regions, (1), (2) and (3). They can physically identified in the following way. Namely, the region (1) is the (bulk+surface) SRH-recombination-limited region with the Fermi level being pinned nearly at its position in the dark, the region (2) is the SRH-recombination-limited region with photo-induced gradual unpinning and the region (3) is the radiationrecombination-limited flat band region, respectively. From this physical interpretation, it is expected that the PL behavior in the regions (1) and (2) is sensitive to the distribution shape and density of surface states. The behavior in these regions can be more clearly by plotting I_{PL}/ϕ and its logarithmic derivative $d(\log(I_{PL}/\phi))/d(\log(\phi))$ vs. ϕ as shown in Fig.l(c) and (d), respectively. For convenience, these plots are hereafter called the PL efficiency spectrum and its derivative spectrum, respectively.

In analyzing the PL efficiency spectra, information concerning of the Fermi level in the dark obviously provides a powerful support. This information can be obtained by the in-situ surface current transport (SCT) measurements which we reported previously.⁴)

3. THEORETICAL CALCULATION OF PL EFFICIENCY SPECTRA

3.1 Method of Calculation

Since the analysis of photoluminescence requires complicated overall selfconsistency among splitting of quasi Fermi levels, band-bending, surface state occupancy and charge, fixed surface charge, electron and hole recombination currents etc., a Sharfetter-Gummel type computer program⁵) including the Shockley-Read-Hall surface recombination process was developed. As the N_{ss} distributions, discrete, uniform and Ushaped distributions were investigated. For the latter two types of distribution, continuous distribution of donor-like bonding states and acceptor-like anti-bonding states below and above the characteristic charge neutrality level, E_{HO}, were assumed in accordance with the unified disorder induced gap state (DIGS) model⁶.

3.2 Calculated PL Efficiency Spectra

Figure 2 shows the calculated PL efficiency spectra for a discrete, uniform and Ushaped distribution of surface states. The calculation was done for the GaAs surface excited by the Ar⁺ laser light (λ =514.5nm). The effect of addition of negative or positive surface fixed charge with the density, Q_{fc}, are also shown in Fig.2.

As seen in Fig.2, the shape of the distribution has a large effect on the efficiency spectra. It has been found that the shape of the spectrum is largely determined by the shape of the N_{ss} distribution, and change in the density magnitude causes a horizontal shift of the spectrum. By taking the derivative spectra of the PL efficiency as shown in Fig.3, the difference in the N_{ss} distribution shape is more clearly reflected in the spectra.

As seen in Fig.2, the surface charge has also a large effect on the PL efficiency spectra. It should be noted that both positive and negative charge enhances the PL efficiency at low excitation intensities. This is caused by the shift of the pinning



Fig.2 PL efficiency spectra for different N_{ss} distributions.



Fig.3 Derivative spectra for PL efficiency in Fig.2.

position towards E_c or E_v . Surface recombination is most efficient when the Fermi level is near midgap, and deviation from midgap towards E_c or E_v reduces the recombination and enhances the PL efficiency. For this reason, a separate information concerning the position of the Fermi level is desirable for an unambiguous interpretation of the PL data.

4. APPLICATION TO EXPERIMENTAL PL DATA

Band edge PL measurements were made at room temperature on variously treated GaAs surfaces and passivated InGaAs surfaces using the Ar⁺ laser light as the excitation source. Measurements were done in the pure nitrogen ambient to avoid possible photo chemical oxidation of the surface during PL measurements.

The measured PL efficiency spectra were compared with the theoretical spectra in Fig.4 for the chemically etched, sulfur $((NH_4)_2S_x)$ treated and thin Au film deposited (100) surfaces of GaAs. The pinning positions of the Fermi level in the dark by the SCT measurements were used for the fitting.

The spectra could be in no way fitted to these assuming discrete distributions. The best result was obtained by assuming a Ushaped distribution shown in the inset.

The results clearly shows that the sulfur treatment does not reduce the N_{ss} , but introduces fixed negative charge, and that deposition of a thin transparent Au film on the chemically etch surface does not appreciably change the N_{ss} distribution.

ciably change the $\rm N_{SS}$ distribution. The measured PL efficiency spectra on the passivated SiO_/InGaAs with and without the ultrathin Si interface control layer (Si ICL)⁷) are compared in Fig.5 with the theoretical spectra using the U-shaped N_{SS} distributions in the inset. The PL measurements were done through the transparent SiO_2 films. The N_{SS} distributions measured on the same structures by the C-V techniques are also shown in the inset. It is seen that agreements between C-V and PL techniques are reasonably good, and that the use of the Si ICL is effective in reducing the interface states.



Fig.4 PL efficiency spectra for GaAs surfaces subjected various treatments.



Fig.5 PL efficiency spectra for passivated InGaAs surface with and without Si ICL.

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