

Characterization of electronic properties of InP(100) surfaces from computer-aided analysis of photoluminescence

MARCIN MICZEK, BOGUSŁAWA ADAMOWICZ

Department of Microelectronics, Institute of Physics, Silesian University of Technology, ul. Bolesława Krzywoustego 2, 44-100 Gliwice, Poland.

HIDEKI HASEGAWA

Research Center for Integrated Quantum Electronics and Graduate School of Electronics and Information Engineering, Hokkaido University, West-8 North-13, Sapporo 060, Japan.

The surface state density distributions $N_{ss}(E)$ on the InP surface were determined by employing a rigorous computer analysis of the dependences of the band-to-band photoluminescence efficiency Y_{PL} versus excitation light intensity Φ . Experimental $Y_{PL} - \Phi$ spectra, taken from the literature, were obtained for the n-InP (100) surface after chemical polishing and ion bombardment. Theoretical $Y_{PL} - \Phi$ curves were calculated using a numerical simulator which takes into account all bulk and surface recombination processes. The $N_{ss}(E)$ distributions were determined for both surfaces from the best fit to experimental data by applying a procedure based on genetic algorithm. An increase in $N_{ss}(E)$ after ion bombardment was attributed to the surface disordering. The behaviour of the effective surface recombination velocity and quasi-Fermi levels for electrons and for holes versus Φ was also analysed.

1. Introduction

Surface states at InP surfaces and interfaces are responsible for many undesirable effects in optoelectronic and high frequency devices, like the Fermi level pinning and large non-radiative surface recombination, which strongly reduces photoluminescence (PL) [1]. Thus, the control and characterisation of the surface state density are the key problems of semiconductor technology. One of the powerful methods of determining the energy distribution of the surface state density $N_{ss}(E)$ on both free and covered surfaces, is the photoluminescence surface state spectroscopy (PLS³) which was developed by the group of Hasegawa [2]. In the PLS³ method, the band-edge photoluminescence efficiency Y_{PL} , *i.e.*, the PL intensity divided by the excitation light intensity Φ , is measured as a function of Φ at room temperature. Then, the obtained $Y_{PL} - \Phi$ spectrum is compared with the theoretical curves rigorously calculated using a numerical simulator of photo-electronic phenomena on a semiconductor surface in order to determine $N_{ss}(E)$ [2] – [4]. The simulator takes

into account all possible recombination processes in the bulk, including band-to-band radiative transitions, Shockley–Read–Hall (SRH) recombination through deep levels and Auger recombination, as well non-radiative recombination at the surface via surface states (in terms of the SRH statistics).

In this paper we applied the PLS³ approach for a quantitative analysis of the $Y_{\text{PL}} - \Phi$ spectra reported by MOISON *et al.* [5] on the n-type InP(100) surfaces submitted to the chemical polishing in bromine-methanol and bombardment by 1 keV argon ions. These treatments are largely used for substrate cleaning before MBE and CVD processes [6]–[8]. For the InP surfaces polished in bromine-methanol high PL [5], [9], [10], low surface recombination velocity S_{eff} [11], and relatively little surface contaminations [6] were reported. It is also known that ion bombardment removes oxygen and carbon contaminations but also amorphises the InP surface region [12]–[15]. In spite of the importance of these procedures in the technology of semiconductor structures, there is little quantitative information about the $N_{\text{SS}}(E)$ distributions on the InP substrates.

We showed that $N_{\text{SS}}(E)$ could be derived from the $Y_{\text{PL}} - \Phi$ spectra measured by MOISON *et al.* [5] in a wide range of Φ (between 10^{20} and 10^{24} photon·cm⁻²·s⁻¹) at room temperature. The authors of [5] presented the analysis of $Y_{\text{PL}} - \Phi$ spectra based on the conventional “dead-layer” model (DLM) for PL. However, DLM cannot explain the rapid increase in Y_{PL} for Φ larger than 10^{22} photon·cm⁻²·s⁻¹, which was observed on the chemically polished surface [5]. Whereas, we obtained a very good modelling of the reported $Y_{\text{PL}} - \Phi$ dependences due to applying rigorous calculations of $Y_{\text{PL}} - \Phi$ curves combined with an optimized fitting. A multi-parameter fitting of theoretical $Y_{\text{PL}} - \Phi$ spectra to experimental data was realised by a newly developed computer procedure based on a genetic algorithm (GA) concept [16]–[18].

We explained the observed evolution of Y_{PL} by a dynamic contribution of surface states to the recombination process. We also determined the U-shaped continuum of surface states $N_{\text{SS}}(E)$ on the studied surfaces. We interpreted an increase in $N_{\text{SS}}(E)$ for the ion-bombarded surface in terms of the surface disordering. Additionally, we analysed the behaviour and correlation of the effective surface recombination velocity and quasi-Fermi levels for electrons and for holes versus Φ .

2. Computation procedure

2.1. Numerical simulator of photo-electronic phenomena

For numerical calculations of the surface quantities versus excitation light intensity Φ we used a one-dimensional Scharfetter–Gummel-type vector-matrix computer program, developed by SAITOH *et al.* [2] for modelling the photon-induced phenomena in a semiconductor. The program self-consistently solves the Poisson’s equation, current equations and continuity equations in a semi-infinite sample and rigorously calculates the electron $n(x)$ and hole $p(x)$ densities, and electric potential

$V(x)$ at a distance x from the surface. Then, for different Φ , the simulator calculates PL quantum efficiency Y_{PL} , the effective surface recombination velocity S_{eff} and quasi-Fermi levels for electrons E_{F_n} and for holes E_{F_p} .

In the calculations, a U-shaped $N_{SS}(E)$ was assumed in accordance with the disorder induced gap state (DIGS) model by HASEGAWA and OHNO [19]. In this model, the fluctuations of bond lengths and angles near a semiconductor surface result in a creation of the localised state continuum in the band gap. The $N_{SS}(E)$ spectrum consists of donor-like states distributed below the so-called charge neutrality level E_{HO} , and acceptor-like ones distributed above E_{HO} . The E_{HO} lies 0.37 eV below the bottom of the conduction band E_C for InP surface. The $N_{SS}(E)$ is expressed by the formula

$$N_{SS}(E) = N_{SS0} \exp \left[\left(\frac{|E - E_{HO}|}{E_{OD,A}} \right)^{n_{D,A}} \right] \tag{1}$$

where N_{SS0} is the minimum surface state density, $E_{OD,A}$ and $n_{D,A}$ are the parameters determining the curvature of $N_{SS}(E)$ function for donor-like states (subscript D) and acceptor-like ones (subscript A), respectively.

The calculations were carried out for the n-type (doping of $3 \cdot 10^{17} \text{ cm}^{-3}$) InP with the bulk lifetime $\tau = 10^{-9} \text{ s}$ [5]. Other necessary bulk InP parameters were taken from [20].

2.2. Fitting procedure

In order to fit the theoretical $Y_{PL} - \Phi$ dependences to the experimental data and to determine the surface state density distribution $N_{SS}(E)$ we developed a multi-parameter fitting procedure. The procedure runs together with the numerical simulator as it is shown in Fig. 1.

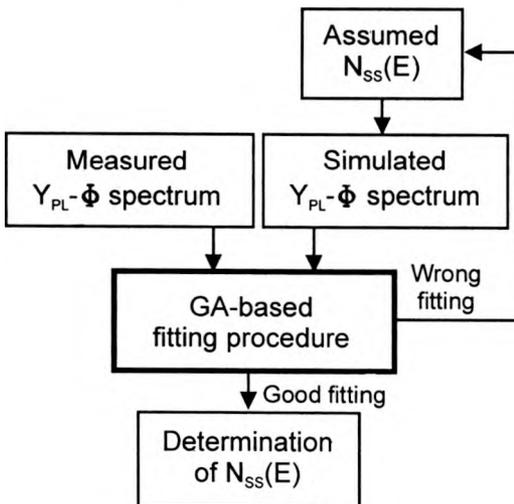


Fig. 1. Flow chart of data analysis procedure in PSL³ method.

The fitting error function (FEF) is defined in accordance with the least-squares method, given by the following relationship [18]:

$$\text{FEF} = \sum_{i=1}^N [Y_{\text{PL}i} - b Y_{\text{PL}}(\Phi_i)]^2 \quad (2)$$

where N is the number of experimental points, $Y_{\text{PL}i}$ and Y_{PL} are the experimental and theoretical values of PL efficiency, respectively, Φ_i is the excitation light intensity applied to the experiment, and b is the scaling coefficient. The coefficient b has been introduced because Y_{PL} is expressed in arbitrary units. For analysis of many $Y_{\text{PL}} - \Phi$ curves measured in the same experimental system, the coefficient b is the same for all curves.

The fitting procedure consists in the search for a minimum value of FEF, *i.e.*, a set of five parameters of the function $N_{\text{SS}}(E)$, ($N_{\text{SS}0}$, E_{OD} , E_{OA} , n_{D} and n_{A}) corresponding to the best fit to the experimental spectrum $Y_{\text{PL}} - \Phi$. In order to solve this optimisation problem, we used in our procedure the genetic algorithm which is based on the natural evolution mechanisms like a selection, crossover and mutation [16], [17]. In our GA-based procedure we use a binary coding of $N_{\text{SS}}(E)$ parameters, a roulette-wheel selection, one-point crossover, and mutation with probability of about 0.04. More details of the procedure one can find in [18]. It should be mentioned that GA has many advantages compared to classical (*e.g.*, gradient) optimisation methods, *e.g.*, GA can avoid local minima of FEF [21] due to simultaneous searching for the best solution over many points.

3. Results and discussion

The experimental dependences $Y_{\text{PL}} - \Phi$ for the chemically polished and ion-bombarded n-InP(100) surfaces taken from [5] and the best fitted theoretical curves obtained from our computer procedure are summarized in Fig. 2a. The best fit was obtained for U-shaped distribution of surface states, $N_{\text{SS}}(E)$, shown in Fig. 2b.

A strong quenching of the Y_{PL} after ion bombardment (by half an order of magnitude under low excitation up to two orders for Φ of 10^{24} photon·cm⁻²·s⁻¹) is caused by the dramatic increase in $N_{\text{SS}}(E)$. The minimum value of N_{SS} increased from 10^{11} to about $3 \cdot 10^{11}$ eV⁻¹ cm⁻², and the density near the band edges rose by two orders of magnitude. In particular, the increase in the branch of acceptor-like surface states near the conduction band results in the larger surface band bending causing the deeper depletion. A similar tendency of surface state density changes estimated from the photoemission measurements was reported by MOISON *et al.* [5]. We attributed the changes in the $N_{\text{SS}}(E)$ distribution to the surface distortion caused by ion bombardment, in accordance with the DIGS model [19].

The increase in disordering of the surface results in the strong change in the behaviour of Y_{PL} versus Φ . The polished InP(100) surface, contrary to that after ion bombardment, exhibited a rapid increase in Y_{PL} for Φ larger than 10^{22} photon·cm⁻²·s⁻¹. We explained this behaviour of PL efficiency by a gradual

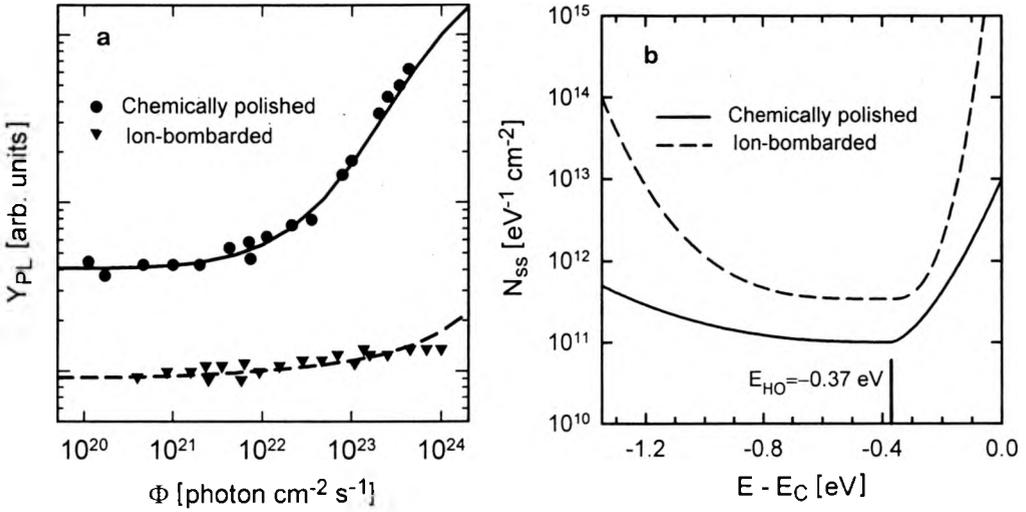


Fig. 2. Calculated PL quantum efficiency Y_{PL} vs. excitation light intensity Φ (a) for $N_{SS}(E)$ (b). Black dots represent experimental data for chemically polished InP(100) surface, and black triangles – for the ion-bombarded surface [5].

saturation of surface states as SRH recombination centers [18], [22]. However, this effect was not observed for the ion-bombarded surface within the used range of Φ .

From our computer analysis, we also estimated the surface state cross-sections for capturing electrons σ_n and holes σ_p . For the chemically polished surface $\sigma_n = 10^{-14} \text{ cm}^2$, $\sigma_p = 10^{-13} \text{ cm}^2$ and after ion bombardment $\sigma_n = \sigma_p = 10^{-13} \text{ cm}^2$. These values are larger than those roughly estimated in the range of 10^{-15} cm^2 by MOISON *et al.* [5]. However, they lie in the range from 10^{-18} to 10^{-12} cm^2 reported in [23]–[27]. A more detailed discussion of an influence of σ_n and σ_p on Y_{PL} one can find in [22].

In order to better understand an influence of the $N_{SS}(E)$ distribution on PL mechanism we calculated the surface recombination velocity S_{eff} and quasi-Fermi levels for electrons E_{F_n} and of holes E_{F_p} in the wide range of Φ (Fig. 3). From the comparison of Fig. 2a and Fig. 3 it is clear that the increasing in Y_{PL} is correlated with light-induced decreasing of S_{eff} and depinning of E_{F_n} . It should be stressed that the DLM approach can be used for the quantitative analysis of PL only in the range of Φ where S_{eff} is Φ -independent and E_{F_n} is pinned.

From Figure 3, it results that S_{eff} on the ion-bombarded surface is about 4 times greater – in the range of low Φ – than on the chemically polished surface, due to higher $N_{SS}(E)$. Furthermore, after ion bombardment, the E_{F_n} pinning position is shifted by about 0.125 eV towards the top of the valence band and also the light-induced depinning of E_{F_n} is slightly weaker in comparison with the chemically polished surface.

Contrary to the E_{F_n} behaviour, the quasi-Fermi level for holes E_{F_p} freely moves within the energy gap due to increasing photo-excitation for both surfaces. One

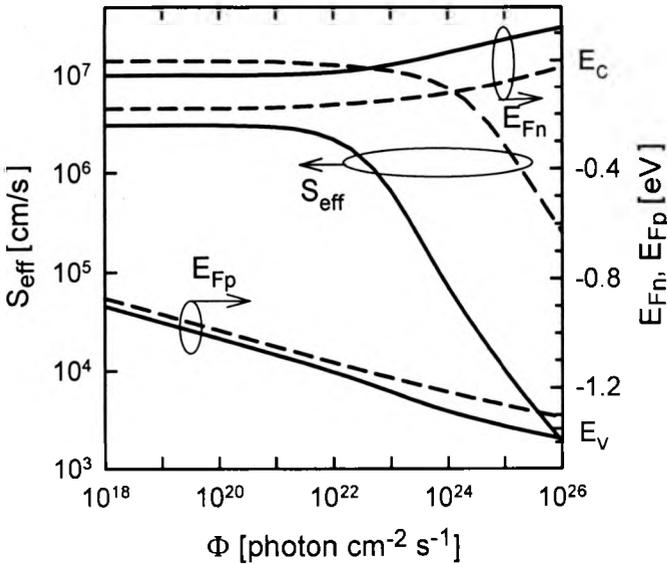


Fig. 3. Effective surface recombination velocity S_{eff} and surface quasi-Fermi levels for electrons E_{F_n} and for holes E_{F_p} vs. excitation light intensity Φ calculated for $N_{\text{SS}}(E)$, as in Fig. 2b.

can note that the difference in E_{F_p} after different surface treatments is apparently smaller than for E_{F_n} . Therefore Y_{PL} quenching on the ion-bombarded surface should be assigned mainly to the majority carrier behaviour related to the stronger depletion of the surface.

4. Conclusions

We performed the rigorous analysis of $Y_{\text{PL}} - \Phi$ spectra measured by MOISON *et al.* [5] for InP surfaces chemically polished and ion-bombarded. Using the GA-based fitting procedure we determined $N_{\text{SS}}(E)$ and estimated σ_n , σ_p for both surfaces. Quenching of Y_{PL} for the ion-bombarded surface can be explained by an increase in $N_{\text{SS}}(E)$ ($N_{\text{SS}0}$ increases 3 times and $N_{\text{SS}}(E)$ increases by about two orders of magnitude near band edges) due to the surface disordering in accordance with the DIGS model. We also analysed the behaviour of S_{eff} , E_{F_n} , and E_{F_p} versus Φ and found correlations with $Y_{\text{PL}} - \Phi$ dependences. Higher $N_{\text{SS}}(E)$ for the ion-bombarded surface results in about 4 times higher S_{eff} and stronger pinning of E_{F_n} .

Acknowledgments — This work was partially supported by the grant 4 T11B 024 23 of the State Committee for Scientific Research (KBN), Poland. The authors (B.A. and M.M.) thank the RCIQE, Hokkaido University, Sapporo for providing the computer simulator for surface analysis.

References

- [1] WADA O, HASEGAWA H., [Eds.], *InP-Based Materials and Devices*, Wiley, New York, 1999.
- [2] SAITOH T., IWADATE H., HASEGAWA H., *Jpn. J. Appl. Phys.* **30** (1991), 3750.

- [3] SAITOH T., HASEGAWA H., KONISHI S., OHNO H., Appl. Surf. Sci. **41/42** (1989), 402.
- [4] ADAMOWICZ B., MICZEK M., IKEYA K., MUTOH M., SAITOH T., FUJIKURA H., HASEGAWA H., Appl. Surf. Sci. **141** (1999), 326.
- [5] MOISON J.M., VAN ROMPAY M., BENSOUSSAN M., Appl. Phys. Lett. **48** (1986), 1362.
- [6] CONTOUR J.P., MASSIES J., SALETES A., Jpn. J. Appl. Phys. Pt. 2 **24** (1985), L563.
- [7] CLAWSON A.R., Mater. Sci. Eng. R **31** (2001), 1, and Refs. herein.
- [8] BRUNI M.R., KACIULIS S., MATTOGNO G., SIMBONE M.G., Vuoto **23** (1994), 89.
- [9] KRAWCZYK S.K., HOLLINGER G., Appl. Phys. Lett. **45** (1984), 870.
- [10] CHANG R.R., IYER R., LILE D.L., J. Appl. Phys. **61** (1987), 1995.
- [11] STURZENEGGER M., PROKOPUK N., KENYON C.N., ROYEA W.J., LEWIS N.S., J. Phys. Chem. **103** (1999), 10838.
- [12] JARDIN C., ROBERT D., ACHARD B., GRUZZA B., PARISET C., Surf. Interf. Anal. **10** (1987), 301.
- [13] THURGATE S.M., ERICKSON N.E., J. Vac. Sci. Technol. A **8** (1990), 3669.
- [14] SMENTKOWSKI V.S., Progr. Surf. Sci. **64** (2000), 1.
- [15] SUNG M.M., LEE S.H., LEE S.M., MARTON D., PERRY S.S., RABALAIS J.W., Surf. Sci. **382** (1997), 147.
- [16] GOLDBERG D.E., *Genetic Algorithms in Search, Optimization, and Machine Learning*, Addison-Wesley, New York 1989.
- [17] MICHALEWICZ Z., *Genetic Algorithms + Data Structures = Evolution Programs*, Springer-Verlag, Berlin 1996.
- [18] MICZEK M., ADAMOWICZ B., HASEGAWA H., Surf. Sci. **507-510** (2002), 240.
- [19] HASEGAWA H., OHNO H., J. Vac. Sci. Technol. B **4** (1986), 1130.
- [20] ADACHI S. [Ed.], *Properties of Indium Phosphide*, EMIS Datareviews Series No. 6, INSPEC, London, New York 1991.
- [21] ULYANENKOV A., OMOTE K., HARADA J., Physica B **283** (2000), 237.
- [22] MICZEK M., ADAMOWICZ B., SZUBER J., HASEGAWA H., Vacuum **63** (2001), 223.
- [23] HATTORI K., TORII Y., J. Appl. Phys. **69** (1991), 3130.
- [24] HE L., HASEGAWA H., SAWADA T., OHNO H., Jpn. J. Appl. Phys. **27** (1988), 512.
- [25] HASEGAWA H., SAWADA T., IEEE Trans. Electron. Dev. **27** (1980), 1055.
- [26] RICARD H., COUTURIER G., CHAOUKI A., BARRIERE A.S., J. Appl. Phys. **62** (1987), 3857.
- [27] RAMPRAKASH Y., BOSE D.N., BASU S., Surf. Sci. **145** (1984), 175.

Received May 13, 2002