Rigorous analysis of electronic properties and AFM studies of oxidising gas sensitive n-InP epitaxial layers

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Abstract This paper deals with both the theoretical and experimental analysis of electronic properties of n-type indium phosphide (n-InP) epitaxial layers covered by native oxides for gas sensor applications. The rigorous calculations of the influence of continuous surface states with U-shaped density distribution \(N_{SSS}(E)\) as well as surface fixed charge \(Q_{FC}\) representing adsorbed ionized species or surface \(\delta\)-doping on the conductivity of n-InP layers were carried out. The surface state density minimum \(N_{SSS0}\) was changed from \(10^{11}\) to \(10^{13}\) eV\(^{-1}\)cm\(^{-2}\). From the Hall effect measurements upon NO\(_2\) exposition the concentration of charge carriers was determined as a function of gas concentration. Additionally, the roughness of the n-InP surface before and after gas action was investigated by using AFM.

1. Introduction
Microstructured devices including MIS capacitors, MISFETs and Schottky diodes based on III-V semiconductors are largely used in the detection of molecular species in gas phase as well as of ions in liquid phase. Recently, the n-InP epitaxial layers were shown to exhibit great sensitivity to oxidizing gases (NO\(_2\), O\(_3\)) [1] of which detection is important for environmental protection. In the case of n-InP based resistive gas sensors, the native oxide layer (that is characterized as being mainly an insulating layer) at the active semiconductor surface is the source of the high density of surface states [2]. It is well known that the surface states at the insulator-InP interface induce many specific effects like surface Fermi level pinning phenomenon and, thus, influence markedly the sensitivity of InP [3] to ion/gas adsorption. Therefore, the comprehension of the influence of interfacial states plays a crucial role in sensing micro-devices technology. However, the standard modelling of semiconductor thin-layer sensors often neglects the impact of intrinsic surface states on the behaviour of the near surface region.

This paper deals with the rigorous theoretical analysis of the n-InP epitaxial layer conductivity as a function of the interface band bending caused by the existence of native oxides. The U-shaped interface state continuum in accordance with a Disordered Induced Gap State model (DIGS) model [4] for semiconductor surfaces and interfaces was used. Such a distribution of surface states has been found experimentally for III-V surfaces covered by native oxides or passivation layer. In our calculation, we used as input parameters the minimum of interface state density, \(N_{SSS0}\), and the thickness of n-InP layer, \(d\). Moreover, the band bending was modified by introducing the surface fixed
charge ($Q_{FC}$) (either positive or negative). In this work, $Q_{FC}$ represents ions adsorbed on the semiconductor surface, which electrostatically changes the band bending or surface $\delta$-doping, both causing large modification of electronic properties of semiconductor surfaces [3]. The experimental studies of electronic properties were realized by means of Hall effect technique. Moreover, the images of the InP surface morphology were realised by Atomic Force Microscopy (AFM) technique and the change in near-surface region after gas action was investigated in terms of surface roughness.

2. Calculation procedure

The rigorous calculations of the conductivity of n-InP layers for different interface states density $N_{SS}(E)$ and fixed charge $Q_{FC}$ were performed using a computer simulator [3]. This simulator uses a one-dimensional Scharfetter-Gummel-type vector matrix algorithm, for the self-consistent solving of Poisson’s equation, current equation and continuity equations for electrons and holes. As a result, the electron $n(x)$, and hole $p(x)$ concentrations and potential, $V(x)$, as a function of the distance $x$ from the surface are obtained. On this basis, the conductivity of the layer is calculated from the standard formula using $n(x)$ and $p(x)$ functions and mobilities of electrons and holes.

The boundary conditions are defined by the surface electric field $E_S = f(N_{SS}(E), Q_{FC})$. For the interface state density distribution, we used the U-shaped DIGS spectrum in the energy gap $N_{SS}(E)$. It consists of the donor-like surface states distributed below the so-called charge neutrality level, $E_{HO}$, and the acceptor-like surface states. The $E_{HO}$ energy is a characteristic value for a given semiconductor because this quantity corresponds to the average orbital energy for sp$^3$ hybrid bonding. Therefore, the position of the $E_{HO}$ level in the energy band gap does not depend on surface treatments and/or the nature of adsorbed ions. For InP, the $E_{HO}$ energy level lies 0.37 eV below the bottom of the conduction band ($E_C$) [4]. The interface state density distribution in the energy gap was expressed by the following formula [3]:

$$N_{SSj}(E) = N_{SS0} \exp \left( \frac{E - E_{HOj}}{E_{Oj}} \right)^{n_j}$$  \hspace{1cm} (1)

where $N_{SS0}$ is the interface states minimum density at $E_{HO}$, the index j corresponds to donor or acceptor like surface state when j=d or j=a respectively. In the calculation we assumed the typical value of the interface state density minimum, $N_{SS0}$ (in the range from $10^{11}$ to $10^{13}$ eV$^{-1}$cm$^{-2}$) for an n-InP layer covered by native oxides. The results were compared with the perfect structure with $N_{SS0} = 0$. Other parameters describing $N_{SS}(E)$ function for n-InP epitaxial layer are: for donor-like states $E_0 = 0.26$ eV, $n = 1.4$ and for acceptor-like ones $E_0 = 0.22$, $n = 3.8$ [3]. The assumed n-type doping was $N_d = 4.6 \times 10^{16}$ cm$^{-3}$ and the thickness of n-InP layer, $d$, was changed from 0.17 to 0.4 µm. The bulk InP electronic parameters were assumed as follows: band gap $E_g = 1.35$ eV, electron and hole mobility: $\mu_n = 3600$ cm$^2$/(V⋅s) [5] and $\mu_p = 150$ cm$^2$/(V⋅s), The simulations were done for the “dark” conditions.

3. Experimental

The measurement set-up used in gas experiments and Hall effect investigation is described in Ref [1]. The Hall effect measurements were performed upon 0.3 Tesla magnetic field and 0.1 mA sample current. The sample tested was a n-InP layer with a thickness of 0.2 µm. As for AFM images were realized by the Nanoscope IIIA multimode made by VEECO Instruments. In AFM experiments the tapping mode was used. The tips were Arrow-Silicon SPM-Sensors produced by Nano world, with a thickness: 4.6 µm, length: 160 µm, width: 45 µm, resonance frequency: 285 kHz and force constant: 42 N/m.

4. Results and discussion

The calculated values of the relative conductivity, $\sigma / \sigma_{NSS0=0}$, as a function of the n-InP layer thickness and $N_{SS0}$ are shown in Figure 1 a). It is evident that the surface states density has a strong influence on the layer conductivity, particularly for the samples with the thickness compared to the depletion region width (d = 0.2 µm) where the ratio $\sigma / \sigma_{NSS0=0}$ is around 0.5. Thus, in microstructured devices based on
InP, the detailed knowledge of the influence of surface states density on material electronic parameters plays an important role, especially in devices based on conductivity or resistivity changes. Figure 1 b) shows the results of calculation of the in-depth profiles of electron concentration $n(x)$ as a function of $N_{SS0}$. It is clear that the interface states create the extended depletion region, which strongly influences the carrier distribution, and thus conductivity of the InP layer, particularly in the case of samples with a thickness in the sub-micron range.

![Figure 1](image1.png)

**Figure 1.** Calculated dependencies of the relative conductivity versus InP layer thickness (a) and in-depth $n(x)$ profiles for different $N_{SS0}$ (b).

Figure 2 shows the calculated changes in InP layer conductivity as a function of the fixed charge density $Q_J/q$. One can observe that the existence of $Q_J$ (which, in practice, may be due to adsorbed ions on the semiconductor surface or surface $\delta$-doping) strongly modifies the conductivity, particularly in the range of accumulation induced by the positive $Q_J$. This marked interface sensitivity to $Q_J$ can be used in optimization of MIS – based sensors and other devices. It should be noticed here that the surface band bending was induced by both the disorder related surface states (DIGS) and the positive or negative $Q_J$.

![Figure 2](image2.png)

**Figure 2.** Calculated dependences of the InP layer conductivity vs the surface fixed charge density $Q_J/q$, for different $N_{SS0}$ and layer thickness.

The described modelling of the surface space charge in InP layers can be used in analysis of the behavior of sensing structures upon gas exposure. Recently we have shown experimentally that oxidizing gas adsorption on n-InP epitaxial layers probably results in the depletion layer development. Our studies regarding the chemical composition changes in the near-surface region due to gas action showed that these changes are over when a stable gas sensor response is obtained. The observed changes in native-oxide layer thickness (before gas action 3.0 nm and after gas sensor response stabilization 3.3 nm [6]) allow us to suppose that the gaseous species modify the surface of InP. On the other hand we suppose that captured electrons origin from the semiconductor bulk. Additional support of this idea we obtained from the Hall effect measurements. Figure 3 depicts changes in the determined electron concentration in a n-InP epitaxial layer as a function of NO$_2$ concentration. One can observe that an increase in gas molecule concentration causes a decrease in the electron concentration due to depletion layer development.
The changes in the native oxide layer were studied in terms of the surface roughness. Figure 4 depicts AFM images before and after gas action. The surface roughness (root mean square) increased after gas action from the value of 0.259 nm before, to 0.771 nm after gas exposure.

5. Conclusion
From the calculations we proved a strong influence of the interface states (with a typical minimum value $N_{SS0}$ in range from $10^{11}$ to $10^{12}$ eV$^{-1}$cm$^{-2}$) on the conductivity of n-InP epitaxial layers with thicknesses in sub-micron range. The n-InP layer conductivity shows also great sensitivity to the surface fixed charge $Q_{FC}$. These properties can be effectively used in the modelling and optimization of microstructured InP-based devices, in particular gas and ion sensors. The Hall effect measurements in terms of electron concentration as a function of gas concentration proved that the gas sensing effect consists in electron capturing from the semiconductor bulk. The change in the surface roughness after gas exposition well shows that gas action caused also the reconfiguration of the surface region, what can be explained by a change in native oxide and a surface contamination layer. The systematic studies of the InP surface electronic status and chemistry as well as the properties of the ohmic contacts are continued in order to better understand the sensing mechanism of investigated sensor structures.

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