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XPS and electric analysis of the GaAs(100) nitridation

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Gallium nitride is the most promising III-V semiconductor, in many applications. Due to its large direct band gap (3.4 eV), GaN can be dedicated as well to optoelectronics devices, e.g. blue lasers and photo-detectors as to the realisation of transistors operating in high-frequency and high-temperature regimes. Therefore, the technology of GaN films on standard substrates, GaAs, attracts special attention. In this paper, nitridation process of GaAs (100) substrates was studied in-situ using x-ray photoelectron spectroscopy (XPS) and ex-situ by means of electrical methods (I-V and C-V) in order to determine chemical, electrical and electronic properties of the elaborated GaN/GaAs interfaces. At first, native oxides were removed from the n-GaAs (100) surface by an argon ion bombardment. Next, a thin film of GaN was obtained by means of the nitridation on the GaAs substrate in an ultrahigh vacuum system using a radio-frequency plasma source (13.56 MHz), which allows nitridation at low pressures (10^{-4} Pa). The Schottky diode (Hg on the fabricated GaN/GaAs structures) was characterised by I-V and C-V analysis. The saturation current I_s, the mean ideality factor n, the barrier height Φ_{BN}, and the serial resistance R_s are determined from the I-V measurements. The C-V curves were controlled by the interfacial state density $N_{SS}(E)$ and by the deep donor levels in the semiconductor bulk. Correlation among chemical, electronic and electrical properties of the GaN/GaAs interface was discussed.

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1. Introduction

A nitridation of GaAs is intensively studied in the last years as the first step of GaN layer deposition or a method for stabilization and passivation of a GaAs surface. Chemical and structural studies on a GaAs surface during and after nitridation (including formation of a GaN/GaAs interface) were performed by many authors[1,2] but the electronic properties of the nitridedGaAs surface in terms of the surface state density distribution, $N_{SS}(E)$, were rarely reported[2].

In this paper, we solved the problem of contactless determination of $N_{SS}(E)$ on GaN/GaAs(100) interfaces using the Photoluminescence Surface State Spectroscopy (PLS^3) method developed in the group of Hasegawa[3,4]. In this technique, the band-edge PL quantum efficiency, $Y_{PL}=I_{PL}/\Phi$ (where I_{PL} is the PL intensity), is measured at room temperature as a function of the excitation light intensity, Φ. Then, the obtained spectrum $Y_{PL}(\Phi)$ is rigorously analyzed using a computer simulator of non-equilibrium phenomena on semiconductor surfaces and $N_{SS}(E)$ is determined from the fitting of theoretical $Y_{PL}(\Phi)$ dependencies to experimental data. We applied the PLS^3 technique for assessment of the electronic status of the nitridedGaAs(100) surfaces covered by GaN layers in terms of the surface state density. The determined value of $N_{SS}(E)$ near the midgap was in the range of 2×10^{11} eV^{-1}cm^{-2}. The low surface state density on the studied samples showed that the applied nitridation technique is a good approach for efficient chemical and electronic passivation of GaAs surfaces.

2. Experimental procedure

Commercially available GaAs(100) wafers have been used in this work. Before introduction in the UHV chamber, the samples are chemically cleaned using successive baths of deionised water, H_2SO_4 and hot propanol. The experiments were carried out in a home-built UHV chamber equipped with XPS (dual anode Al-Mg X-ray source and hemispherical energy analyser). XPS experiments were performed using a Mg Kα source (1253.6 eV) at an incident angle of 65° (normal detection, pass energy of the analyser equal to 30 eV). The substrates were cleaned using 1 keVAr+ ions with a current of 6 μA at 6.10^{-5}Torr. GaAs substrates were nitridated using a home made double stage differential pumping RF plasma cell at a temperature equal to 500°C (the sample was heated from the back by an electron beam bombardment): N_2 gas was introduced in the plasma cell and pumping into the preparation chamber, the pressure was 10_{-}^{4}Pa. After nitridation, GaN deposition was achieved using a Knudsen-type gallium source with a quartz balance for measurement of deposition rate.

Two samples were made. The sample A is obtained after two hours GaN deposition. The sample B is heated again at 600 °C after two hours GaN deposition.

Electrical measurements are made with temporary mercury gate of 1.5 mm diameter. The current-voltage I-V curves were obtained using a HP Semiconductor Parameters Analyser 4155B.

3. X-ray Photoelectron spectroscopy

After in situ Ar^+ionic etching of GaAs substrates, XPS Ga3d peak shows that there is no evidence of metallic gallium on the surface.

Fig. 1 shows the Ga3d spectrum for sample A. This peak contains two contributions (FWHP = 2.44 eV) : the first one is a gaussian peak at a binding energy of 19 eV, which represents Ga-As bonds and the second one corresponding to Ga-N bonds at a binding energy of 19.8 eV [5,6].

The Ga3d spectrum, after 2 hours annealing at 600°C, is presented in the Fig. 2. It can be fitted with only one Gaussian peak (FWHP = 1.9 eV) at a binding energy of 19.8 eV, which represents Ga-N bonds. Then, the annealing of the sample at 600 °C makes it possible to improve the formation of a homogeneous layer of GaN at the surface.

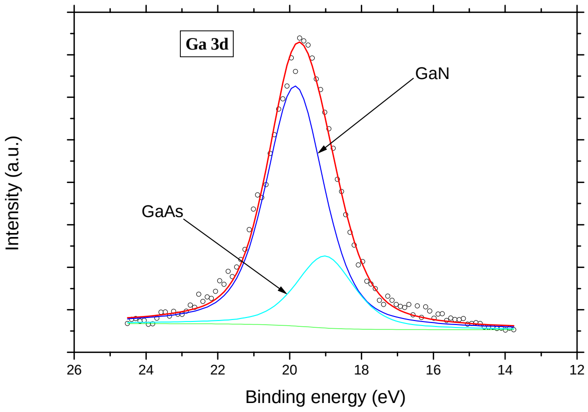

Fig. 1 :Ga3d core-level spectra for sample A.

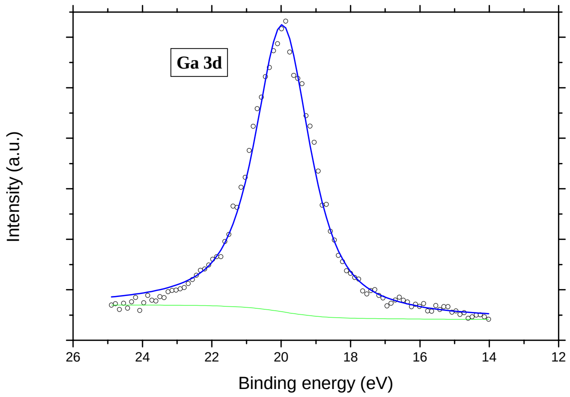

Fig. 2. Ga3d core-level spectra for sample B.

4. Electrical measurements

The Hg/GaN/GaAsSchottky diode were characterised by electrical measurements (I-V and C-V). The measurements of the forward current-voltage and backward current-voltage I-V of Hg/GaN/GaAs samples are shown in the Fig. 3. The direct currents have exponential forms, however, the direct current for the sample annealing at 600 °C (sample B) is higher than that for the sample no heated. A great difference appears for the reverse current. For the sample B, the reverse current is more important than that for the sample A.

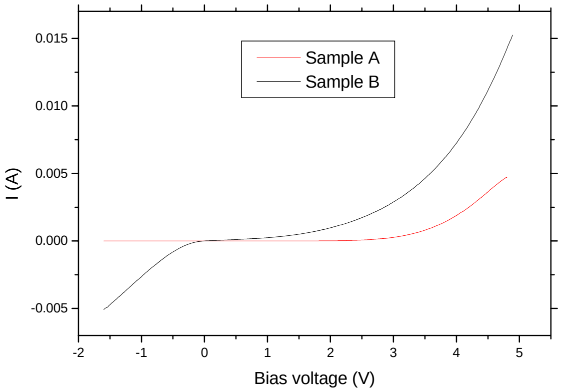

Fig. 3. Current-voltage characteristic of the Hg/GaN/GaAs samples.

The determination of the electrical parameters was achieved using the characteristic formula expressing the current through a Schottky diode: [7,8]

$$I(V) = I_s \times \exp\left(\frac{q \times (V - R_s \times I)}{n \times k_B \times T}\right) \quad (1)$$

where: q, T, V, n and $R_S$are the magnitude of the electron charge, the temperature in Kelvin, the applied voltage, the mean ideality factor and the serial resistance respectively. The saturation current I_S is given by[7,8]:

$$I_s = S \times A^* \times T^2 \times \exp\left[-\frac{q}{kT} \times \Phi_{Bn}\right] \quad (2)$$

A^*, S and Φ_{Bn} are the Richardson constant, the area of the rectifying contact and the barrier height respectively. From the $\ln\left[I \Big/ \left(1 - e^{-qV/kT}\right)\right] = f(V)$ curves, we have estimated the saturation current I_S and the ideality factor n. By substituting the values of I_S in Eq. (2), we have deduced the height of the potential barrier Φ_{Bn} which is increase from 0.45 eV from sample A to 0.53 eV from sample B. This values are comparable with that obtained by [9], which is equal to 0.52 eV for Sn/n-GaAsSchottky diode. The incrementation of Φ_{Bn} after annealing is confirmed by[10].When the current becomes somewhat high, we must take into account the voltage between the terminals of the series resistance R_S [11]. The energy of the interface states E, relative to the conduction band edge E_c at the semiconductor surface, is given by [11] :

$$E_c \quad E = q \times \left(\Phi_{Bn} \quad V\right) \tag{3}$$

The density of the interface state N_{ss} related to the interface state capacitance C_{ss} is given by [11]:

$$C_{ss} = \frac{S \times q \times N_{ss}}{w \times \tau} \times arctg\left(w \times \tau\right) \tag{4}$$

where w is the width of the space charge zone and τ is the relaxation time of the interface state and is defined as follow[11]:

$$\tau = \frac{1}{V_{th} \times \sigma_n \times N_d} \times e^{q \times V_d / kT} \tag{5}$$

whereN$_d$ and V_d are the doping concentration and the diffusion potential, respectively, σ_n represents the cross-section of the interface states and V_{th} is the thermal velocity of the carriers ($V_{th} \approx 10^7$ cm s^{-1}).

For a Schottky diode with a thin interfacial layer between the metal and the semiconductor and at sufficiently high frequencies such that the interface states cannot follow the AC signal, the slope of the C^{-2} (V) relationship obtained by [12]is given by:

$$\frac{dC^{-2}}{dV} = \frac{2}{q \times \varepsilon_s \times N_d} \times \left[\frac{C_{sc} + C_i}{C_{sc} + (1 + \alpha) \times C_i}\right] \tag{6}$$

whereC$_i$ and C_{sc} are the interfacial layer and depletion zone capacitances, respectively. The parameter α is given by [12]:

$$\alpha = \frac{q \times N_{ss} \times \delta}{\varepsilon_i} \tag{7}$$

The presence of a thin interfacial layer δ implies that $C_i >> C_{sc}$, Eq. (6) can be reduce to:

$$\frac{dC^{-2}}{dV} = \frac{2}{q \times \varepsilon_s} \times \left[\frac{1}{N_d \times (1 + \alpha)}\right] \tag{8}$$

According to relation (8), the slope of the high frequency C^{-2}(V) is constant if the interfacial states density N_{ss} is constant.

The presence of deep donor levels in the semiconductor bulk gives an important value of the interfacial state density which is evaluated using the C-V curve measured at 1 MHz. Then, it is equal for the two samples and is estimated to 4 × 10^{11} eV^{-1} cm^{-2} at the midgap (see Fig. 4). This value is very interesting and predict realisation of electronic (GaN/GaAs) devices with good performances.

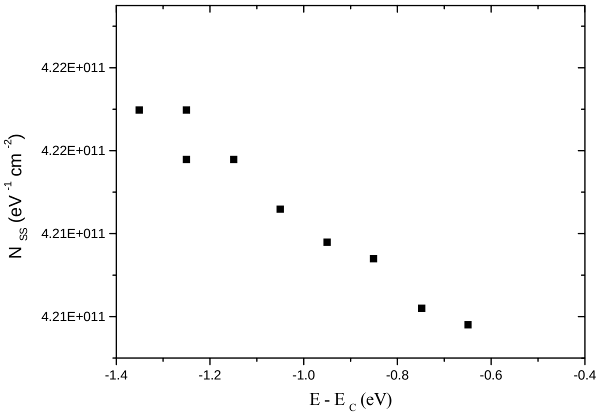

Fig. 4. Distribution of state density in the band gap.

The electrical parameters calculated from I(V) and C(V) curves are summarised in Table 1.

Table 1 : Electrical parameters obtained for Hg/annealing(GaN/GaAs)and Hg/no heated (GaN/GaAs) structures.

	I_S (A)	Φ_{Bn} (eV)	V_d (V)	R_S (Ω)	n	N_{SS} (eV^{-1}cm^{-2})
Sample A	2.5 × 10^{-5}	0.45	3.26	85	1.26	4 × 10^{11}
Sample B	3 × 10^{-5}	0.53	3.3	95	1.3	4 × 10^{11}

5. Photoluminesence analysis

Photoluminescence from the nitridedGaAs samples was measured at room temperature in the Institute of Electron Technology (Warsaw, Poland) in the standard PL setup using the green line (514.5 nm, 2.41 eV) of an argon laser for excitation. The obtained experimental PL efficiency spectra $Y_{PL}(\Phi)$ are presented in figure 5. It is worth mentioning that the PL intensity was very high despite the fact that the samples had been kept in air for several weeks before PL measurements. Furthermore, a dynamic evolution of Y_{PL} (increase by about 4 times) in a very small range of Φ cannot be explained by the standard simplified so-called 'dead-layer' model of PL in semiconductors [13].

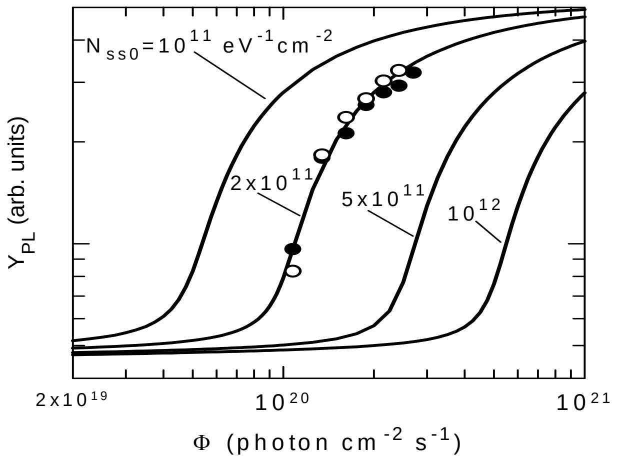

Fig. 5. The experimental PL efficiency spectrum measured from the nitridedGaAs (filled circles (sample A) – emptycircles (sample B) and theoretical spectra (lines).

In order to rigorously calculate theoretical $Y_{PL}(\Phi)$ spectra, one should consider an extremely complicated situation in a semiconductor under photo-excitation. Namely, excess carriers split electron and hole quasi-Fermi levels and dynamically modify the occupation of surface states. The surface states change band bending through their charge and cause the recombination of carriers. In addition to the surface recombination, the bulk SRH (Shockley-Read-Hall) recombination, radiative recombination giving rise to photoluminescence, and Auger recombination take place. All these phenomena are analyzed self-consistently by a one-dimensional Scharfetter-Gummel-type vector-matrix computer program, developed by [3].

In the calculations, we assumed a U-shaped continuous distribution of surface state density $N_{SS}(E)$ in accordance with the Disorder Induced Gap State (DIGS) model, developed by [14]. The calculations were carried out for n-doped (N_D=1.4×10^{18} cm^{-3}) GaAs. Other necessary surface and bulk GaAs parameters were taken from references [15,16].

We obtained a very good fitting of the theoretical $Y_{PL}(\Phi)$ curve to experimental data (figure 5) for the surface state density distribution $N_{SS}(E)$ showed in figure 6. The low surface state density N_{SS} was obtained i.e. the minimum in the range of 2×10^{11} eV^{-1}cm^{-2} and $N_{SS}(E)$ below 10^{14} eV^{-1}cm^{-2} close to the bands. These results are comparable to those reported by Anantathanasarn and Hasegawa for the Si_3N_4/GaN/GaAs structure fabricated on the nitridedGaAs[2].

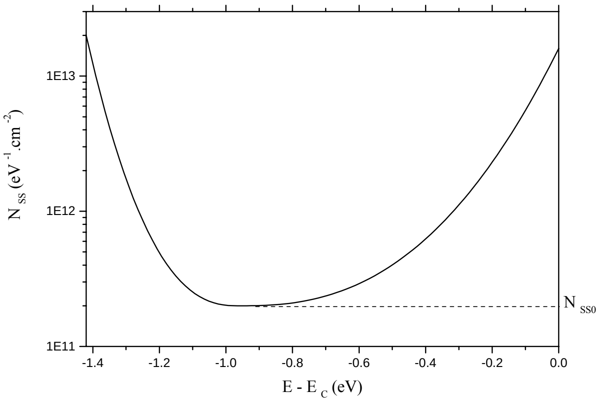

Fig. 6. Distribution of state density in the band gap obtained by photoluminescence analysis.

From Fig. 5, it is evident that Y_{PL} depends on both surface state density as well as excitation light intensity, Φ, and is Φ-independent only for low excitations. The increase of Y_{PL} for higher Φ can be explained by a gradual saturation of the surface states as recombination centers.

6. Conclusion

Native oxides were removed from the n-GaAs (100) surfaces by an argon ion bombardment. Next, a thin film of GaN was obtained by means of the nitridation on the GaAs substrate in an ultrahigh vacuum system using a radio-frequency plasma source (13.56 MHz), which allows nitridation at low pressures (10^{-4} Pa). The XPS analysis shows that the annealing of the sample at 600 °C makes it possible to improve the formation of a homogeneous layer of GaN at the surface.The Schottky diode (Hg on the fabricated GaN/GaAs structure) was characterised by I-V and C-V analysis. The saturation current Is, the mean ideality factor n, the barrier height Φ_{Bn}, and the serial resistance R_S are determined from the I-V measurements. These values show that the annealed sample is more efficient than the unannealed sample. This result is in agreement with XPS measurements.

The interfacial state density is evaluated using the C-V curves. Then, it is equal to 4×10^{11} eV^{-1} cm^{-2} at the midgap. This value is very interesting and predict realisation of GaN/GaAs devices with good performances.

The surface state density distribution $N_{SS}(E)$ was determined on the nitridedGaAs(100) surface using the PLS^3 technique. The value of the interface state density $N_{SS}(E)$ close to the midgap was estimated to be in the range of 2×10^{11} eV^{-1}.cm^{-2}, indicating a good electronic quality of the obtained interfaces. This value is in a good agreement with the value obtained by C-V measurements.

The rigorous analysis of the dynamics of $Y_{PL}(F)$ spectra revealed that the studied GaAs samples were well passivated in terms of the low density of the surface states. This result can be attributed to good chemical properties of the obtained overlayers which seem to be nearly-stoichiometric GaN films with little oxygen contaminations. However, the insulating properties of the GaN layers should be improved for future applications in MIS structures.

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