JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 11 No 5, 05007(5pp) (2019)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 11 № 5, 05007(5cc) (2019)

Effect of Porous GaAs Layer Morphology on Pd/porous GaAs Schottky Contact

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(Received 27 April 2019; revised manuscript received 25 October 2019; published online 25 October 2019)

GaAs:Sn – GaAs:Si samples with a porous layer formed on their surfaces have been explored. The porous layer was formed by electrochemical anodization of the surface of n-GaAs:Si sample in HF:C_2H_5OH = 1:1 under 3 min etching time and etching current variation within the range of 20-80 mA. Schottky AgPd contact across the porous layer was formed by electron-beam evaporation, AgGePd ohmic contacts to *n*+ GaAs:Sn were formed by electron-beam evaporation followed by annealing. It has been identified that an increase in the anodizing current density leads to an increase in the uneven structure of the porous layer, and when the current density is greater than 60 mA/cm^2, clusters are formed as a result of fragmentary separation of the porous layer from the substrate. The spectral analysis has proved that PL intensity increases with porosity growth. We believe that this effect is due to the fact that the average size of the micropores and the amount of material remaining in the layer decrease with increasing layer porosity. To identify the influence of the porous layer morphology on the Schottky contact parameters, the *I-V* characteristics of the structures have been explored. It has been discovered that with increasing layer porosity, the difference in characteristics between the structure without porous GaAs and structures with porous GaAs increases, that results in decreasing direct current and increasing reverse current. This can be explained by the decrease in the porous GaAs layer, and, as a consequence, by the decrease in the charge carrier density. The Schottky barrier height for Pd/porous GaAs with different morphology of the porous layer was calculated. It has been found out that the Schottky barrier height increases from 0.65 to 0.73 eV with a porous layer thickness. It has been established that the increase in the porous layer thickness leads to the rise of the ideality factor, which grows from 1.24 to 1.7 with the layer height and results in a deterioration of Schottky contact parameters.

Keywords: Schottky contact, Porous layer, GaAs, Ideality factor.

DOI: 10.21272/jnep.11(5).05007 PACS numbers: 85.30.Hi, 85.40.Xx, 07.07.Df

1. INTRODUCTION

Gallium arsenide coated with a porous layer (porous GaAs) makes devices with specific properties possible to be produced [1]. Among other applications of porous GaAs are humidity and gas (e.g. CO, CO_2, NO, NO_2 and so on) sensors, which can operate at room temperature and have fast response speed [2, 3]. Many such devices apply the Schottky contact across porous GaAs for gas control [4]. In [5], the effect of the Schottky barrier height on the sensitivity to various gases has been explored. The papers state that the Schottky barrier height changes when the sample is affected by gas, which leads to the variation in the current-voltage (*I-V*) characteristic of the Schottky contact. Thus, it can be stated that the sensitivity and speed of such sensors directly depend on the Schottky barrier height, which forms the electrical properties of the Schottky contact.

The formation of Schottky contacts across GaAs is described in details in [6], at the same time the formation of the Schottky contact across porous GaAs has its own characteristics related to the morphology of the contact area, which, for porous GaAs, is not polished mechanically or chemically, that affects the interlayer resistance.

Various metals are used to form Schottky contacts across GaAs and porous GaAs, the most often are Pd, Pt and Au [7]. For porous GaAs sensors, Pd and Au [8] are used to form the Schottky contact but with different methods of porous GaAs surface metallization. However, the influence of the porous layer structure on the electrical properties of the Schottky contact is not studied enough.

As a rule, a porous layer on the GaAs surface is obtained by the method of electrochemical etching in an acidic medium [9]. In this method, the porous layer structure is defined by the etchant composition, etching current and etching time. This paper presents the research of the morphology effect on I-V characteristics of the Schottky contact across porous GaAs with different porous layer morphology obtained by various etching current under fixed time and etchant composition. The solution of this problem will allow optimizing the parameters of gas sensors based on porous GaAs with Schottky contacts. For comparison, Schottky contacts across GaAs and porous GaAs have been explored in the paper.

2. DESCRIPTION OF EXPERIMENTAL SAMPLES MANUFACTURING

In this work, GaAs:Sn – GaAs:Si epitaxial samples of crystallographic orientation (100) have been used. Samples are made of GaAs:Sn plates with 400 μm thick-ness of 10^{18} cm^{-3} carrier concentration (n^+-GaAs:Sn layer) measured by the Hall method with a Hall-200 unit. Then the plates were surfaced by gaseous epitaxy with a 20 μm GaAs layer of 10^{16} cm^{-3} carrier concentrations (*n*-GaAs:Sn layer) guaranteed by the manufacturing technology. The conductivity type of the obtained layers was identified by the hot probe method on a TP-201 installation. In total, 5 structures have been explored, and 4 samples have been surfaced with a porous layer.

Before the porous layer and ohmic contacts have been formed, the samples had been degreased by successive immersions in organic solvents of trichlorethylene, acetone, methanol, then washed with dionized water and dried with dry nitrogen for 10 min.

An ohmic contact of AgGePd-GaAs with layer thicknesses of 100/50/10 nm, respectively, and subsequent annealing for 30 min at 350 °C has been formed across the *n*+-GaAs:Sn layer by the method of electron-beam evaporation.

A porous layer with an area of 6.28 cm^2 has been formed in an electrolytic cell using HF:H_2O (1.5:1) etchant as it has been suggested in [10]. The anodization current density varied in the range of 20-80 mA at anodization time of 3 min. The etching area was illuminated by 100 W halogen lamp.

The porous layer surface has been explored using MII-4 microinterferometer microscope with a 500x optical magnification equipped with a DLT-Cam digital microscopy camera and DLTCamViewer software using an OM-O micrometer object for software calibration. Quantitative analysis of the porous layer was performed on a ZEISS EVO 50XVP scanning electron microscope equipped with an INCA-energy 450 detector. The layer porosity was calculated by the gravimetric method on AXIS ANG200C scale.

AgPd/GaAs and AgPd/porous GaAs Schottky contact was formed by the electron-beam evaporation.

3. RESULTS AND DISCUSSION

Let us consider the study of a porous layer on n-GaAs surface used in this work. As mentioned above, 4 structures have been prepared at various anodizing current. The current density during samples anodizing is 20, 40, 60, 80 mA/cm^2. The surface of the porous GaAs layer has been studied well enough with SEM [11] and AFM [12]. In our work, for analyzing the surface of a porous layer over a large area, we have used an optical microscope with 500 x magnification, which made 150 x 150 µm porous layer possible to explore. The images are shown in Fig. 1.

As a result, we can state that the increase in current density leads to higher nonuniformity of the porous layer structure that supports those in [13]. When the current density is more than 60 mA/cm^2, the formation of clusters is observed because of the fragmentary porous layer peeling from the substrate.

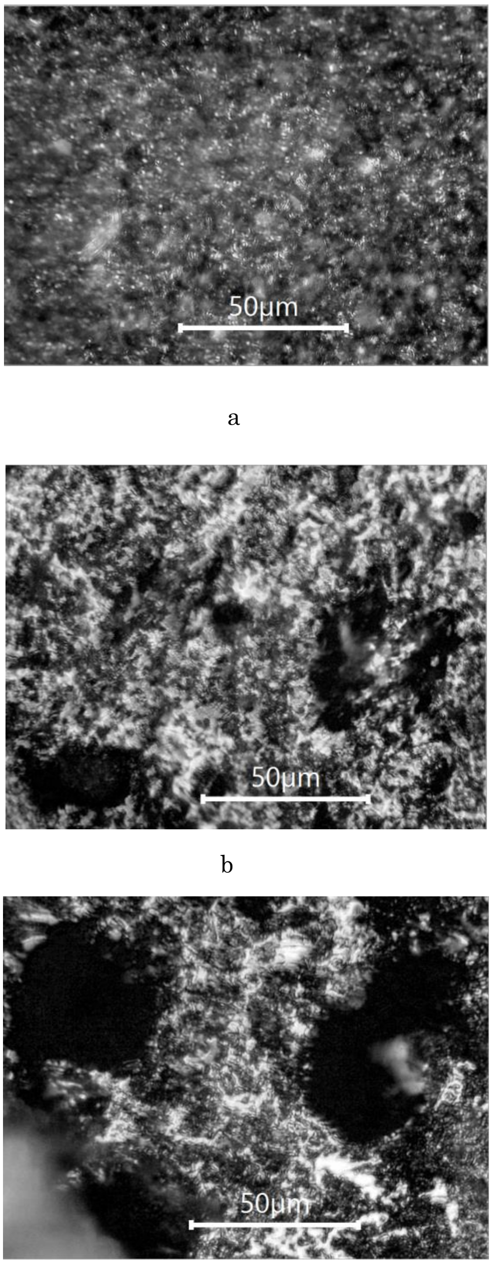
The porosity has been calculated by the gravimetric method. The authors of [14] describe the gravimetric method for porous silicon and propose the following equation:

$$P(\%) = \frac{(m_1 - m_2)}{(m_1 - m_3)}, \tag{1}$$

where m_1 is a mass of the sample before anodization, m_2 is a mass of the sample after anodization, m_3 is a mass of the etched porous layer. The porous layer is etched with NaOH aqueous solution.

The etching of the porous GaAs layer causes certain technological difficulties; therefore, in the work, the porosity was determined with the equation:

$$P(\%) = \frac{(m_1 - m_2)}{\rho S h} \times 100\%, \tag{2}$$



a

b

c

Fig. 1 – Optical images of the porous GaAs layer with 500x magnification, 3 min anodizing time and the current density: 20 mA/cm^2 (a); 60 mA/cm^2 (b); 80 mA/cm^2 (c)

where ρ is GaAs density ($\rho = 5.32$ g/cm^3), S is an area of the porous GaAs layer (6.28 cm^2), h is a height of the porous layer.

The porous layer height was taken by optical measurement of the fracture of additional samples, on which a porous layer was created under identical anodizing modes. The measurements were carried out with DLTCamViewer software by computing the pixels on the fracture with MII-4 microscope comprising DLT-Cam digital camera.

The results of the calculation of samples porosity are given in Table 1.

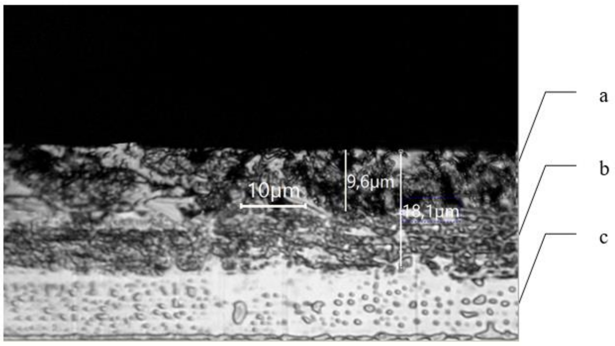


Fig. 2 – Optical image of the sample fracture with 500x magnification of porous GaAs layer anodized at 80 mA/cm^2 current density and 3 min anodizing time: porous GaAs layer of 10 μm height (a), n-GaAs:Si layer (b), n^+-GaAs:Sn layer (c)

Table 1 – Results of structures porosity calculation

No	Sample mass before anodizing, m_1, g	Sample mass after anodizing, m_2, g	Porous layer height, cm·10^{-4}	Porosity, %
1	1.0222	1.0215	1	45
2	0.8897	0.8822	4	57
3	1.1429	1.1269	7	70
4	1.0145	0.9872	10	83

To analyze the morphology of porous GaAs layers, the photoluminescence spectra have been studied in accordance with [15]. Photoluminescence (PL) was excited by a laser with 405 nm wavelength. The PL spectra have been measured at room temperature. While the obtained layers were exciting with PL, bright radiation was detected in the green-yellow wavelength range.

The microstructure of the glow region is fairly uniform, and the radiation intensity is stable over time. For all layers, there is a shift of the IR maximum to the shortwave region of the PL spectrum. All porous GaAs samples have demonstrated PL in the visible region of the spectrum, and the dependence of the intensity and shape of the PL spectra on the uniformity of the porous layer surface and its height, which in turn are determined by the anodizing modes (Fig. 3), has been observed. Analysis of the spectra has indicated that the PL intensity increases with increasing porosity. This is due to the fact that with an increase in the porosity of the layer, the average size of micropores decreases and the amount of material remaining in the layer decreases.

In our opinion, minor differences in the maximum intensity of the radiation spectrum at wavelengths in the range of 500-600 nm for samples obtained at etching current density of 60-80 mA/cm^2 (samples 3 and 4) compared with samples 1 and 2, have been caused by clusters of destroyed porous layer (see Fig. 1b, c).

To estimate the effect of the porous layer morphology on Schottky contact parameters, the current-voltage (*I-V*) characteristics of the studied structures with and without a porous layer have been constructed.

Fig. 4 presents *I-V* characteristics of Pd/n-GaAs and Pd/porous GaAs Schottky contacts for the samples. From the figure, *I-V* characteristics of all samples have obvious differences in both direct and reverse branches.

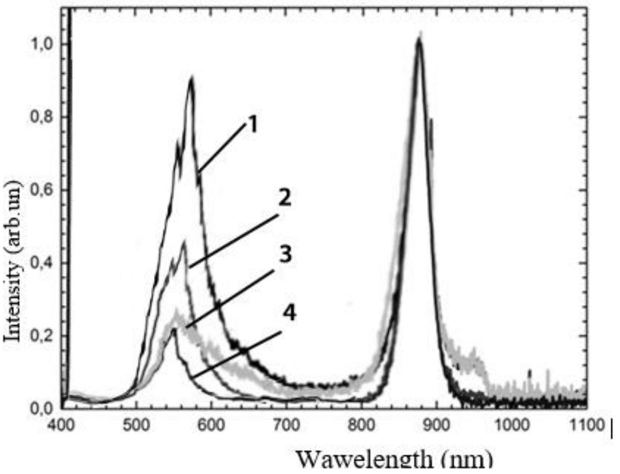


Fig. 3 – PL spectra of porous GaAs layers obtained by varying the anodizing current density: 20 mA/cm^2 (1), 40 mA/cm^2 (2), 60 mA/cm^2 (3), 80 mA/cm^2 (4)

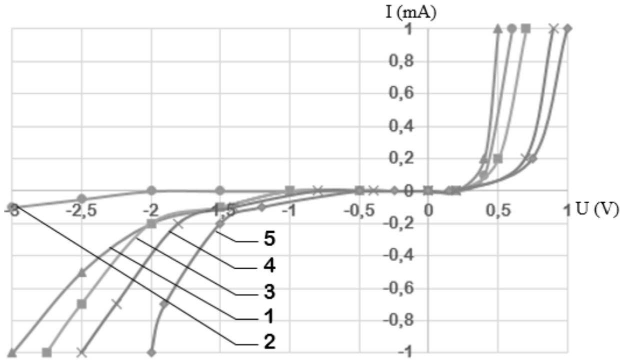


Fig. 4 – *I-V* characteristics for the Pd/GaAs and Pd/porous GaAs samples: Pd/GaAs (1), Pd/porous GaAs 20 mA/cm^2 (2), Pd/porous GaAs 40 mA/cm^2 (3), Pd/porous GaAs 60 mA/cm^2 (4), Pd/porous GaAs 80 mA/cm^2 (5)

I-V characteristics analysis in Schottky contacts of the metal – porous semiconductor – semiconductor type is discussed in detail in [16]. Analysis of *I-V* characteristics shows the differences increase in *I-V* characteristics of the sample without a porous layer and one with porous GaAs while layer porosity growing. It appears in decreasing forward current and increasing reverse current. An obvious explanation for this dropping is that the porous layer consists of pores where charge carriers are absent, so differences in the *I-V* characteristics increase with higher porosity.

Based on the expressions given in [17] and obtained *I-V* characteristics, Schottky barrier parameters were calculated, particularly the Schottky barrier height (ϕ_b), ideality factor (n) and series resistance (R_s) for every sample. The results are summarized in Table 2.

In our opinion, the increase in Schottky barrier height with growing porosity is caused by different rates of Ga and As etching while forming a porous layer, which is proved by the quantitative analysis, the results of which are shown in Fig. 5.

The analysis proves that with porosity increase in the porous layer columns, Ga percentage becomes higher and As percentage – lower. For the sample anodized at 80 mA/cm^2 current density, porous GaAs columns

Table 2 – Parameters of the Schottky barrier of Pd/GaAs and Pd/porous GaAs samples

Sample	**Ideality factor (n)**	**Series resistance (R_s), Ω**	**Schottky barrier height (ϕ_b), eV**
Pd/GaAs	1.1	1.7	0.65
Pd/porous GaAs (1)	1.24	1.76	0.68
Pd/porous GaAs (2)	1.35	1.78	0.69
Pd/porous GaAs (3)	1.5	1.8	0.7
Pd/porous GaAs (4)	1.7	1.87	0.72

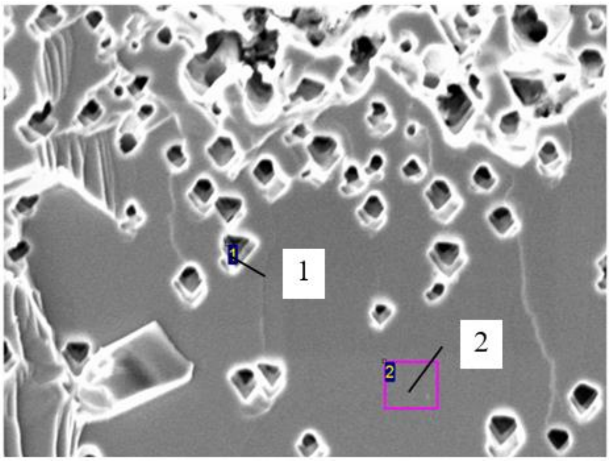


Fig. 5 – Quantitative analysis of Pd/porous GaAs sample anodized at 80 mA/cm² current density and 3 min anodizing time

consist of 62 % Ga and 38 % As (zone 1 in Fig. 5) while the substrate consists of 49 % Ga and 51 % As.

Since the As electron work function is within 4.79-5.11, the Ga work function is within 3.96-4.16 and the work function of GaAs is 4.64, it can be stated that the higher the Ga percentage in the porous layer, the lower the porous GaAs work function, which leads to an increase in Schottky barrier height.

From the data in Table 2, the ideality factor remains greater than unity for Pd/GaAs and Pd/porous GaAs contacts. Obviously, this is due to defects caused by the presence of a thin insulating layer, an oxide layer formed involuntary in manufacturing the contacts between palladium and *n*-GaAs or porous GaAs. Indeed, it is assumed that both contacts behave like a metal/interlayer/semiconductor configuration, where the interphase layer causes a voltage drop across the intercontact layer. It can be stated that the ideality factor of Pd/porous GaAs is higher than that of Pd/*n*-GaAs and depends on the anodizing mode, which is obviously due to the heterogeneity of Pd/porous GaAs interlayer. The series resistance is close to 2 Ω for the Pd/*n*-GaAs and Pd/porous GaAs structures, which is lower than it has been calculated in [18].

The high ideality factor can be explained by the sum of ideality factors of porous GaAs/GaAs heterojunction and metal/porous GaAs Schottky barrier. Moreover, porous GaAs has a large effective surface area and, therefore, the high concentration of unsaturated bonds acting like the high concentration of carrier traps in porous GaAs. Consequently, porous layers with high resistance make a significant contribution to the high dynamic series resistance of the metal/porous GaAs/GaAs/metal structure.

4. CONCLUSIONS

The influence of the morphology of the porous n-GaAs layer on the characteristics of Pd/porous GaAs Schottky contact has been explored. Four samples of the GaAs:Sn – GaAs:Si structures have been studied. For manufacturing a porous layer on n-GaAs:Si layer, the porous layer morphology has been varied. To estimate the parameters of Schottky contacts, the *I-V* characteristics have been measured, the ideality factor and the series resistance have been calculated. The Schottky barrier height for Pd/porous GaAs with different morphology has been calculated, and Schottky barrier height increases from 0.65 to 0.73 eV.

It has been established that Schottky barrier height grows with increasing porosity because of a decrease in As percentage with a high electron work function and an increase in the Ga percentage with a lower work function, which leads to a decrease in the electron work function of the porous layer columns.

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Вплив морфології поруватого шару GaAs на параметри контакту Шотткі паладій / поруватий GaAs

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В роботі досліджувалися структури GaAs:Sn – GaAs:Si, на яких формувався поруватий шар. Поруватий шар отримували електрохімічним анодуванням в HF:C2H5OH = 1:1 при часу анодування 3 хв і варіацією струмів анодування в діапазоні 20-80 мА. До поруватого шару створювався контакт Шотткі AgPd методом електронно-променевого напилення, омічні контакти AgGePd до n^+-GaAs:Sn створювалися методом електронно-променевого напилення з наступним відпалом. Показано, що збільшення щільності струму анодування призводить до підвищення нерівномірності структури поруватого шару, і при щільності струму більше 60 мА/см^2 спостерігається утворення кластерів, викликане фрагментарним відшаруванням поруватого шару від підкладки. Аналіз спектрів показав, що інтенсивність ФЛ збільшується з ростом поруватості. В роботі показано, що даний ефект викликаний тим, що зі збільшенням пористості шару зменшується середній розмір мікропор і зменшується кількість GaAs, що залишився в шарі. Для визначення впливу морфології поруватого шару на параметри контакту Шотткі були досліджені вольт-амперні характеристики структур. Показано, що зі збільшенням поруватості шару відмінність в характеристиках між структурою без поруватого шару GaAs та структур з поруватим шаром GaAs зростає, що проявляється у зниженні прямого струму і збільшенні зворотного, що пояснюється зменшенням товщини поруватого шару, і як наслідок зниженням щільності носіїв заряду. Визначено висоту бар'єру Шотткі для Pd/поруватий GaAs з різною морфологією і встановлено збільшення висоти бар'єру від 0,65 до 0,73 eВ зі збільшенням товщини поруватого шару. Встановлено, що збільшення товщини поруватого шару призводить до збільшення фактора ідеальності, який з ростом висоти шару збільшується від 1,24 до 1,7 і як наслідок призводить до погіршення параметрів контакту Шотткі.

Ключові слова: Поруватий шар, Арсенід галію, Контакт Шотткі, Фактор ідеальності.