Research of the solar-blind and visible-blind photodetectors, based on the AlGaN solid solutions

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Abstract. The paper is devoted to the development and study of solar-blind and visible-blind photodetectors. We report on the spectral characteristics of the ultraviolet photodetectors based on Shottky barrier to the epitaxial layers of the n-Al$_x$Ga$_{1-x}$N solid solutions. The use of Schottky barrier photodiodes is advantageous since it does not require the growth of additional epitaxial layer of $p$-type conductivity.

1. Introduction

Currently ultraviolet (UV) photodiodes are of great interest. There are several types of such photodiodes. Let us consider several variants and their main drawbacks. SiC-based photodiodes have a relatively narrow range of sensitivity. GaP photodiodes have a good signal to noise ratio but it is impossible to create solar-blind and visible-blind photodiodes based on them without the use of filters. Si-based photodiodes also requires expensive optical filters for registration shortwave signals against the backdrop of strong illumination by visible light. From this point of view, the most promising material for short-wavelength photodiodes is a solid solution Al$_x$Ga$_{1-x}$N [1]. In particular, the material system AlN-GaN forms a series of direct-gap solid solutions that allow creating photodiodes with sharp wavelength edge of photosensitivity in a given region, including solar- and visible-blind ones. In addition, the nitrides have high chemical resistance and good thermal stability which allows devices based on them to be used in extreme conditions [2].

Solar-blind and visible-blind photodiodes are used in the wavelength ranges less than 290 nm and 360 nm, respectively, and have no sensitivity outside these spectral ranges. For example, they can be applied in the military industry as solar-blind sensors registering flame radiation from a missile against the backdrop of exceeding background illumination by the visible light. Visible-blind photodiodes can be used for studying ozone layer depletion where the amount of ultraviolet radiation is greatly increased [3, 4]. The use of Si photodiodes for such applications is unreasonable because they are much more responsive to both visible and infrared spectral ranges and require expensive optical filters. Furthermore, it is often impossible to choose an optical filter with transmission in the required spectral range.

The use of Schottky barrier photodiodes is more advantageous, since it does not require an additional epitaxial $p$-type layer [5, 6]. The paper demonstrates the technology for creating visible-
blind and solar-blind nitride-based photodiodes on the basis of a relatively simple and low-cost hydride vapor phase epitaxy (HVPE).

Photodiodes based on Schottky barrier are easier to build than photodiodes based on p-n-junction. However, such structures do not require light to penetrate into the bulk of the semiconductor as the absorption occurs at the metal-semiconductor interface. However, despite all the advantages of photodiodes based on epitaxial layers of solid solutions \( \text{Al}_x \text{Ga}_{1-x} \text{N} \) there are still some not fully solved problems. In particular, there are difficulties in growing epitaxial layers of \( \text{Al}_x \text{Ga}_{1-x} \text{N} \) with high Al content. High dislocation density leads to high values of leakage currents and may affect the short-wavelength edge of the photosensitivity, as well. In this paper, we report on the structures grown by two epitaxial methods: 1. Structures based on the top epitaxial layer \( \text{Al}_{0.1} \text{Ga}_{0.9} \text{N} \) were grown by HVPE.

2. \( \text{Al}_x \text{Ga}_{1-x} \text{N} \) structures with Al content in the range of \( 0.1 < x < 0.6 \) were grown by molecular - beam epitaxy (MBE).

2. Sample and experimental technique

The photodetectors were formed by the epitaxial layers grown by two methods: MBE with plasma activation of nitrogen in the metal-rich conditions, and HVPE [8] on the \( \text{Al}_2 \text{O}_3 \) (0001). The use of the \( \text{Al}_2 \text{O}_3 \) substrate having a good crystalline affinity for materials III-N as well as relatively thick AIN buffer layers provides a higher quality of the surface structure. The introduction of three-stage AIN buffer layer and AIN/AlGaN short-period lattice at the early growth stages provided satisfactory structural quality of the layers having dislocation density of \( 10^8 - 10^{10} \text{ cm}^{-2} \). The studies of the kinetics of AlGaN layers growth under metal-rich conditions when the total flow ratio of III group elements to the flow of activated nitrogen \( F_{\text{III}} / F_{\text{N}} \approx 1.5 - 2 \) showed that the surface became atomically smooth, even at relatively low growth temperatures of 700 °C. An additional advantage of the metal-rich conditions is the possibility to control Al content in the layers as equation \( x = F_{\text{Al}} / v_{\text{AlGaN}} \) is valid in this mode, wherein \( F_{\text{Al}} \) - calibrated Al flow, \( v_{\text{AlGaN}} \) - measured growth rate of the layer which is determined by the active nitrogen flow, i.e. \( v_{\text{AlGaN}} = F_{\text{N}} \). In the same mode the \( \text{Al}_x \text{Ga}_{1-x} \text{N} \ (x = 0 – 0.65) \) layers were grown (Fig. 1).

![Figure 1. The structure of \( \text{Al}_x \text{Ga}_{1-x} \text{N} \) samples grown by MBE.](image)

The high dislocation density as well as the high manufacturing costs of layers growing by epitaxial methods (molecular-beam epitaxy, vapor phase epitaxy from metal-organic compounds) create not high-quality and cheap photodetectors. The samples grown by HVPE were studied in order to address above-mentioned issues. This method has a number of technological advantages over MBE and allows significant reduction of the production cost of \( \text{Al}_x \text{Ga}_{1-x} \text{N} \) solid solutions epitaxial layers. In particular, the HVPE produces epitaxial layers of high crystalline quality at the same time providing the ability to control the rate of growth over a wide range: from a fraction of a micron to tens and hundreds of
micrometers per hour. The dislocation density in the used samples ranged from $9 \cdot 10^7$ cm$^{-2}$ to $8 \cdot 10^8$ cm$^{-2}$.

The photodetectors based on metal-semiconductor contact were created according to the method for vacuum thermal resistive deposition of metal on the Al$_x$Ga$_{1-x}$N solid solution epitaxial layers (Fig. 2).

![Figure 2](image_url)

**Figure 2.** The structure of Al$_x$Ga$_{1-x}$N samples grown by CHVPE.

The contacts were created by vacuum thermal deposition. The Ti/Al structure, where Ti is a sublayer for Al, was used as an ohmic contact. Such metals as Au, Ni, Ag, In, Sn were deposited up to thickness of 15 nm for the Schottky barrier. During deposition the substrate was heated up to 300°C.

The study of the spectral characteristics was performed with the use of a diffraction grating monochromator having a light source on the basis of a xenon lamp with a bulb absorbing no UV radiation component.

### 3. Experimental results and discussions

Figures 3 and 4 show the spectral characteristics of UV photodiodes test structures, their long-wavelength sensitivity limit can be determined by the bandgap of the forbidden region of the Al$_x$Ga$_{1-x}$N solid solution. Fig.3 illustrates the use of the Al$_x$Ga$_{1-x}$N solid solution with the aluminum content of $x = 0.08$ that allows creating a visible-blind UV detector. Such a detector is sensitive within the 200 - 360 nm wavelength range. Furthermore, it is almost insensitive to radiation wavelength over 370 nm that allows detecting UV radiation under a strong ambient illumination by visible light. Fig. 3 shows that the Au-based Schottky barrier photodiode has a sensitivity from 210 to 360 nm, FWHM of 50 nm and the maximum photoresponse at 320 nm. The use of Ni as a translucent contact has extended the sensitivity range that was within 200 - 360 nm with a maximum photoresponse at 300 nm. The FWHM of the sensitivity spectrum of Ni-Al$_{0.08}$Ga$_{0.92}$N-based structure was equal to 95 nm. The spectral operational range of the Ni-based photodiode is the same as for Ag photodiode but its FWHM is 10 nm less and is equal to 85 nm. The wavelength of maximum sensitivity is 285 nm (Fig. 3).
The increase in the aluminum content enabled the shift of the sensitivity edge to shortwave region, including a "solar-blind" photodetector at a value of $x = 0.38$ (see Fig. 2.4). The red edge of solar-blind UV photodiode is 290 nm. At $x$ values higher than 0.8 the sensitivity range of Al$_x$Ga$_{1-x}$N structure would be in the vacuum UV r with the wavelength less than 200 nm.

Figure 4 shows that the FWHM of Au-Al$_{0.38}$Ga$_{0.92}$N structure is 50 nm at maximum photosensitivity of 265 nm. The Ni- and Ag-based photodetector has approximately the same value of FWHM (about 35 nm), however, the maximum photosensitivity for Ni-based Schottky barrier is 270 nm and it is shifted to 4 nm relative to the maximum for Ag.
The studies have demonstrated that the greatest sensitivity is revealed by the Au-contact structure (Fig. 5), in particular, the value of the Au-Al\textsubscript{0.08}Ga\textsubscript{0.92}N Schottky barrier photoresponse is 9 times higher than that one of the Sn-based diode, and 1.6 times higher than that of Ni-Al\textsubscript{0.08}Ga\textsubscript{0.92}N.

The quality of the metal-semiconductor interface and the associated surface recombination sufficiently affects the sensitivity of the shortwave edge. In Au-based structures border was the most biased toward higher energies region that indicates the low surface recombination velocity. This fact considerably determines the sensitivity of gold based structures.

![Graph](image1)

**Figure 5.** The spectral characteristics of photodetectors based on Schottky barrier to the Al\textsubscript{1-x}Ga\textsubscript{x}N with different metal of Schottky barrier.

Pretreatment of the semiconductor surface significantly affects the sensitivity of the photodiodes based on Schottky barrier. To study this effect we washed the structures with acids and alkalies (see Table 1) for 1 minute before metal deposition. Table 1 also shows the influence of the amount of chemical reagent on the value of maximum photosensitivity ($I_{\text{max}}$). Changing the position of the photoresponse maximum ($\lambda_{\text{max}}$) is associated with the composition fluctuations of the solid solution on the substrate.

| Surface treatment         | $\lambda_{\text{max}}$, nm | $I_{\text{max}}$, a. u. |
|---------------------------|-----------------------------|------------------------|
| KOH+H\textsubscript{2}O   | 337                         | 0.224                  |
| HF (20%)                  | 338                         | 0.214                  |
| HNO\textsubscript{3}:HCl  | 335                         | 0.197                  |
| HCl+H\textsubscript{2}O   | 339                         | 0.144                  |
| CCl\textsubscript{4}      | 336                         | 0.142                  |
| H\textsubscript{3}PO\textsubscript{4} | 333               | 0.088                  |
| H\textsubscript{2}SO\textsubscript{4}:H\textsubscript{3}PO\textsubscript{4}:H\textsubscript{2}O | 337 | 0.072 |
| as grown                  | 334                         | 0.041                  |
It was established that the surface pretreatment in KOH allows the increase in photosensitivity by 5.5 times as compared with untreated surfaces. Close parameters demonstrated structures processed in HF (see Table 1).

4. Conclusion
The experimental samples were created of UV photodetectors based on metal-solid $n$-$Al_{x}Ga_{1-x}N$ solutions with various $x$ aluminum content. We established that the heat treatment of the gold contact structure provides 4 time increasing in photosensitivity. We observed that the pre-clean parameters of the epitaxial layer surface have the most important influence on the contact characteristics. Heating is essential for a better adhesion of the metal to the surface of the epitaxial layer. We demonstrated that the heating temperature during the deposition of the sample is tol be 300 °C. The contact thickness should be 15 nm in order to meet the translucent effect. It was established that the surface pretreatment in KOH allows the increase in photosensitivity by 5.5 times as compared with untreated surfaces.

The gold translucent contact provided a high photosensitivity along with the other advantages such as oxidation resistance, high conductivity, and performance ability. This leads to the most perspective use thereof in creating the studied photodiodes.

On the basis of $n$-$Al_{x}Ga_{1-x}N$ solid solution with aluminum content of $x = 0.08$ we succeed in creating a visible-blind UV detector. Such a detector is sensitive in 200 - 360 nm wavelength range. The increase in Al content up to 0.38 allowed us to implement a pilot solar-blind UV photodiode having the spectral sensitivity region that lies within the range of 200 - 290 nm. The photodiode has no sensitivity to the radiation wavelength exceeding 300 nm.

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