

Effect of nitride chemical passivation of the surface of GaAs photodiodes on their characteristics

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Abstract. Characteristics of GaAs photodiodes have been studied before and after the chemical nitridation of their surface in hydrazine sulfide solutions, which leads to substitution of surface As atoms with N atoms to give a GaN monolayer. The resulting nitride coatings hinder the oxidation of GaAs in air and provide a decrease in the density of surface states involved in recombination processes. The device characteristics improved by nitridation are preserved during a long time.

1. Introduction

Monolayer gallium nitride (GaN) layers formed on the surface of GaAs crystals can serve for an effective chemical and electronic passivation of the surface of semiconductor devices based on these crystals. Owing to the high strength of Ga – N bonds, coherent nitride coatings exhibit a chemical stability sufficient for protecting the GaAs surface from being oxidized in air. This precludes the appearance of intraband surface states characteristic of the oxidized GaAs surface. These states create parasitic conductance channels on the surface of structures with p – n junctions, such as photodiodes. In addition, when surface arsenic atoms are replaced with the substantially more electronegative nitrogen, newly formed surface states fall deeper into the valence band of GaAs and become electrically inactive. Thus, the surface recombination rate substantially decreases in a nitridized crystal [1], which, in turn, markedly improves the surface – dependent electronic and optical characteristics of the given semiconductors. The present study is concerned with the influence exerted by the chemical surface passivation on the efficiency of GaAs photodiodes, associated with the minimization of the leakage current due to the tunnel – trap (excess) and recombination charge transport mechanisms.

2. Sample fabrication

GaAs photodiode (PD) p – i – n structures were fabricated in two stages by liquid – phase epitaxy and Zn diffusion. Lightly doped n⁰ – GaAs layers were epitaxially grown from a Ga – As melt in the hydrogen atmosphere at temperatures of 750 to 700 °C. To reduce the content of residual impurities in the n⁰ – GaAs layers being grown, minor amounts (up to 0, 05 at %) of rare – earth elements (Yb, Sc, Er, Y) were added to the Ga – As melt [2, 3]. The free electron concentration in the n⁰ – GaAs layers was in the range from 1×10^{14} to 5×10^{15} cm⁻³. The diffusion of zinc was performed on the surface of an epitaxial layer to form a p⁺ layer with a hole concentration of about 5×10^{19} cm⁻³ [4]. PD chips had



the form of mesa structures with ring-shaped ohmic contacts fabricated by optical lithography and wet etching down to the substrate.

The GaAs surface was nitridized by its treatment in a buffer solution of hydrazine hydrochloride in hydrazine hydrate (pH = 8,5) containing sodium sulfide [5, 6] in a concentration of 0,01 M.

After the natural oxide layer is removed in the alkaline medium, arsenic atoms on the GaAs surface selectively interact with SH^- anions, which results in that molecules of thioarsenic acid are formed and electrophilic adsorption centers appear on exposed gallium atoms. Then, mutually competing processes of adsorption of univalent OH^- and SH^- anions and nucleophilic hydrazine molecules present in the alkaline sulfide solutions develop on these centers. Although the primary coverage of gallium atoms is predominantly formed via chemisorption of univalent anions, the ability of nucleophilic nitrogen atoms in hydrazine (N_2H_4) molecules to successively form two or three bonds with electrophilic gallium atoms provides to these atoms the possibility of an irreversible substitution of the chemisorbed anions. Depending on the coordination of the incorporated nitrogen atoms, determined by the initial crystallographic orientation of the GaAs surface, doubly coordinated amino groups NH or triply coordinated nitrogen atoms remain on the surface after the final dissociation of the adsorbed hydrazine molecules. Thus, the GaAs (111) B, (100), and (110) surfaces and those with intermediate crystallographic orientations are terminated with electronegative nitrogen atoms, which form substantially stronger chemical bonds with gallium atoms, compared with arsenic atoms. In this case, it can be said that a solid GaN layer coherent with the crystal is formed. As a result, the nitrogen-related surface states are localized within the valence band of GaAs and become electrically inactive, and the surface of the nitridized crystal becomes resistant against oxidation by atmospheric oxygen. At the same time, in the case of the gallium (111) A surface, treatment in a hydrazine sulfide solution yields an adsorption layer composed of sulfur dimers that pairwise bind gallium atoms [6]. This coating also provides an electronic passivation and chemical stability of the GaAs (111) A surface. Consequently, irrespective of the set of orientations of the facets forming the mesa structures, their treatment in hydrazine sulfide solutions leads to a stable electronic and chemical passivation of the intricate surface of a gallium arsenide device structure.

3. Results and discussion

Forward dark current – voltage $J - U$ characteristics and external quantum efficiency spectra were measured for GaAs PDs before and after the surface nitridation. The forward dark $J - U$ characteristics were measured at room temperature at current densities $J = (10^{-9} - 1) \text{ A/cm}^2$ and voltages $U = (0 - 1, 5) \text{ V}$. The external quantum efficiency spectra were measured at wavelengths $\lambda = (350 - 900) \text{ nm}$.

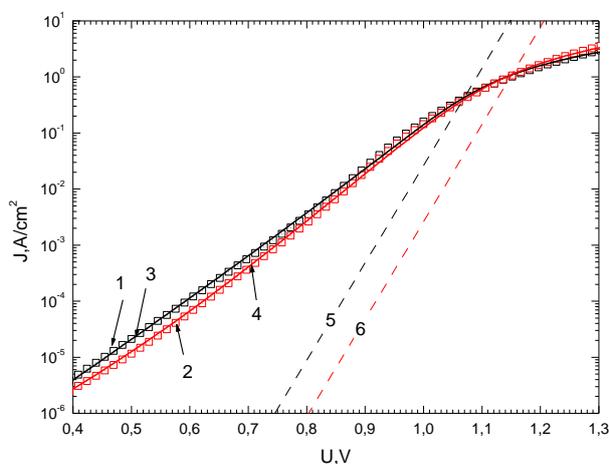


Figure 1. Forward dark current – voltage characteristics of GaAs photodiodes: (1, 2) experimental; (3, 4) calculated before and after the deposition of GaN, respectively; (5, 6) calculated exponential curves corresponding to the diffusion charge transport mechanism, $A = 1$ (Shockley), $J_{0d} = 1,1 \times 10^{-19}$ and $1,1 \times 10^{-20} \text{ A/cm}^2$ before and after the deposition of GaN, respectively.

Figure 1 shows calculated and experimental forward dark $J - U$ characteristics before and after the surface nitridation of GaAs PDs. Analysis of the forward dark $J - U$ characteristics, carried out using method described in [7, 8], shows that the pre-exponential factor J_{0d} corresponding to the diffusion charge transport mechanism with $A = 1$ (Shockley) decreased by an order of magnitude, from 10^{-19} to 10^{-20} A/cm², after the experiment in which a GaN monolayer was formed.

It follows from the results of measurements of the external quantum efficiency spectra (in figure 2) that the sensitivity of the photodiode increases by more than 8% at wavelengths of 400 – 870 nm after its surface is nitridized.

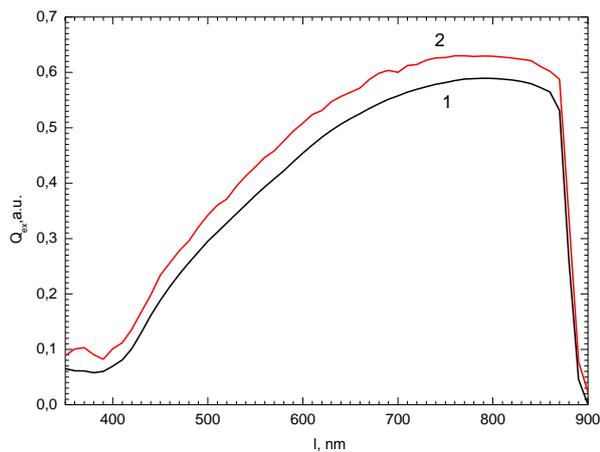


Figure 2. Spectra of the external quantum efficiency Q_{ext} of the GaAs PDs under study: (1) before and (2) after the deposition of a GaN monolayer.

4. Conclusion

A method was suggested for producing a gallium nitride monolayer on the side and front surfaces of GaAs PDs via chemical nitridation in hydrazine sulfide solutions.

Forward dark current – voltage characteristics and external quantum efficiency spectra were measured for GaAs PDs before and after the nitridation. An analysis of the characteristics before and after the nitridation of the front and side surfaces of GaAs PDs in hydrazine sulfide solutions demonstrated that the method suggested for producing a gallium nitride monolayer provides the following:

- The pre-exponential factor of the dark $J - U$ characteristic, which corresponds to the diffusion charge transport mechanism with $A_d = 1$ (Shockley), decreases by an order of magnitude, from 10^{-19} to 10^{-20} A/cm².
- The external quantum efficiency increases by more than 8% at wavelengths $\lambda = 400 - 870$ nm.

Acknowledgments

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