Optical properties of plasmonic metal nanoparticles on GaN surface

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Abstract. Effect of the plasmonic resonant absorption in metal nanoparticles formed on the GaN surface on optical properties of samples is studied. Silver and gold nanoparticles are formed by solid-state dewetting on epitaxial GaN grown by molecular beam epitaxy (MBE) on c-sapphire substrate. Theoretical and experimental optical characteristics show the appearance of characteristic absorption of the surface plasmon resonance. The results of the work show the possibility of increasing the efficiency of GaN-based optoelectronic devices.

1. Introduction

Gallium nitride (GaN) is widely used in modern innovative electronics as the base material for light-emitting diodes (LED), lasers, photo-detectors and other high-power and high-frequency devices [1, 2]. Attention to this material is due to the combination of its physical properties such as wide and direct bandgap, high breakdown voltage, and high effective mobility of charge carriers, good thermal conductivity, and chemical inertness [3]. GaN based photo detectors are considered as promising devices in UV spectral range (wavelength λ<365 nm). The wide bandgap provides high selective photosensitivity in UV which makes it possible to avoid the installation of any additional optical filters absorbing visible and infrared spectral parts.

Recently, metal nanoparticles (NPs) have been proposed as a viable tool to improve the performance of optoelectronic devices due to their plasmonic behavior [4-6]. Such structures are capable of exhibiting the effect of localized surface plasmon resonance (LSPR), which is widely used for tuning of optoelectronic processes in photovoltaics [7], photocatalysis [8], and photodetectors [9] due to improved optical absorption and / or charge transfer [10]. The most common materials used to make nanoparticles are silver [11], aluminum [4], platinum [5] and gold [6] because of their high optical activity.

In this study, the plasmon effect leading to the capture of photons in the process of localized scattering is studied in detail, which increases the time of interaction of light and material. The efficiency of the electro-optical conversion can be increased by enhanced interaction stimulating by scattering.

2. Experimental

Highly conductive GaN layers were synthesized by molecular beam epitaxy with plasma nitrogen activation (MBE PA) on semi-insulating 2 um thick [0001] GaN layer pre-grown by MOCVD on c-Al2O3 substrate. The surface GaN/Al2O3 plate was cleaned according to the protocol developed by us (see details in [12]). Samples were placed to the Veeco Gen 200 industrial-type machine immediately after the cleaning. 300 nm thick silicon-doped GaN layers were grown by the PA MBE at constant
values of the substrate temperature $T_s = 700 \, ^\circ C$. The gallium flux $F_{Ga}$ was $\sim 0.25 \, \mu m/h$, and an activated nitrogen flux $F_N$ was $\sim 0.05 \, \mu m/h$. The silicon flux used during the MBE PA synthesis made it possible to obtain the electron concentration in GaN layer of $\sim 3.7 \times 10^{18} \, cm^{-2}$, as it was previously established in [12]. The formation of metal nanoparticles was carried out by the solid state dewetting using the technique described in [13]. Metallic films of Au and Ag were deposited on the surface of the epitaxial GaN layer by vacuum thermal evaporation. The thickness of the films was 1.5 and 3 nm for both metals. The formation of nanoparticles was carried out by high-temperature annealing at 550 °C in an air ambient for 60 minutes.

The simulation of the optical characteristics of an array of metal nanoparticles on the GaN surface was carried out using Comsol Multiphysics software by the full-wave equation solution as described in [14]. Uniform distribution of metal nanoparticles on the GaN surface was assumed in order to somehow simplify calculation. Thus, the simulation was carried out on one hexagonal-shaped simulation cell containing the stack Sapphire/GaN/metal NP/air with periodic boundary conditions applied in all lateral directions of the cell. The metal nanoparticle was modelled as a 30 nm diameter hemisphere, which is consistent with the structures made under similar technological conditions [15]. GaN optical parameters (refractive index, extinction coefficient) were taken using data for similar epitaxial layers [16, 17]. Metal nanoparticles were described using the Drude-Lorenz model [18].

The morphology of the epitaxial GaN film, metal films and the distribution of metal nanoparticles were studied by SEM using Supra 55VP setup. The elemental composition of the samples was determined by EDS technique. The photoluminescence spectra of the structures were measured using an Accent RPM Sigma setup with 266 nm laser pumping at low power. Optical transmittance and reflectance spectra were measured using AvaSpec-ULS2048XL-EVO-RS spectrometer with a xenon light source. The rough back surface of the c-Al$_2$O$_3$ substrate was coated with immersion liquid GEM-A 1.79 R.I to eliminate undesirable light scattering. The equality of the refractive indices of the liquid and the sapphire substrate makes it possible to exclude the rough interface of the sapphire substrate.

3. Results

Figure 1 presents plan-view and cleavage edge images of GaN samples obtained by SEM. It can be seen in these images the absence of a pronounced interface between the surface of the GaN/c-Al$_2$O$_3$ substrate and the upper GaN layer grown by the PA MBE. At the same time, on the surface of the GaN layer synthesized by the MBE PA method, a relatively high density of V-shaped defects is observed. These defects have a characteristic shape of inverted hexagonal pyramids, which can be formed around dislocations seeded at the sapphire substrate and threading through all GaN layer. Also, the data obtained using the SEM indicated that the total thickness of the GaN epitaxial layer is about 2.1 - 2.4 μm. The upper GaN layer grown by the PA MBE method has the thickness of ~ 300 nm over the entire substrate area.

The spectral characteristics of the transmission, reflection and absorption of the sample with epitaxial layers before metal deposition are shown in the Figure 2. The resulting films have high transparency in the visible and IR spectral ranges and high absorption at wavelengths below 370 nm. Analysis of the interference peaks of the spectral characteristics confirmed the thickness of the epitaxial layers. The numerical simulation results showed good agreement with the measured spectra. However, the obtained samples show a sharper absorption edge.

EDX analysis of the elemental composition after the samples after thin Au and Ag film deposition confirmed their presence on the GaN surface. At the same time, depending on the thickness, the quantitative ratio differed twofold, which correlated with the parameters of the technological process. Figure 3 shows SEM images of samples after metal deposition. For samples with a metallization thickness of 1.5 nm, both for Au (Figure 3a) and Ag (Figure 3c), a nonuniform metal distribution over the GaN surface is seen. Formation of individual nanoparticles is clearly observed. At the same time, for samples with a thickness of 3 nm, coverage is better and a sort of cluster structure instead of nanoparticles is seen (Au Figure 3b; Ag Figure 3c).
Figure 1. Plan-view and cleaved edge SEM images of the GaN/c-Al₂O₃

Figure 2. Experimental and theoretical reflection and absorption transmission spectra of GaN / c-Al₂O₃ substrate

Figure 3. SEM image of GaN surface after metal film deposition: (a) Au 1.5 nm; (b) Au 3 nm; (c) Ag 1.5 nm; (d) Ag 3 nm.

Figure 4 shows the photoluminescence spectra of virgin GaN sample and samples covered with thin metallic films. It can be seen from the Figure 4 (a) that an 1.5 nm Au film has almost no effect on the band-to-band PL intensity, in contrast to a thicker gold film. Silver affects it much effectively, which can be explained by the higher activity of Ag in the UV spectral range. In this case, the dumping of PL intensity is approximately proportional to the film thickness. After high-temperature annealing, a significant decrease in band-to-band PL intensity is observed on all samples with a metal coating (Figure 4b). No clear dependence of PL on the film thickness is seen after annealing. At the same time, an increase in the photoluminescence intensity is observed in the yellow spectral range for samples coated with Ag, which is primarily seen for a thinner coating.
Figure 4. Photoluminescence spectra of virgin epitaxial GaN and samples coated with a thin metal film: (a) before; and (b) after high temperature annealing.

A preliminary analysis of the spectral characteristics of metal nanoparticles on a GaN/c-Al$_2$O$_3$ substrate by numerical methods showed the appearance of their plasmon behavior (Figure 5).

Figure 5. Calculated spectral characteristics of metal nanoparticles on a GaN / c-Al2O3 substrate: (a) AuNP; (b)AgNP

Figure 6 shows the experimental transmission and reflection spectra of the Au / GaN / c-Al$_2$O$_3$ (a) and Ag / GaN / c-Al$_2$O$_3$ (b) samples after high-temperature annealing in comparison with the initial GaN / c-Al$_2$O$_3$ substrate. For samples with AuNP, a good agreement with the numerical model, where plasmon resonance is observed at wavelengths of 550 and 600 nm (Figure6a) is seen. In addition, an increase in absorption in the UV part of the spectrum is observed. However, no plasmon peaks were observed in the spectral characteristics of Ag-coated samples after annealing (Figure 6b), with the same increase in absorption in the UV part of the spectrum. This can be caused by a change in composition of the silver coating during high-temperature annealing in the air. Silver nanoparticles could be fully oxidized during annealing.

4. Conclusion

The effect of plasmonic resonant scattering in metal nanoparticles formed on the surface of silicon-doped GaN is studied. Epitaxial silicon doped GaN layers are grown on the GaN surface of MOCVD-GaN / c-Al2O3 substrate by the PA MBE. Silver and gold nanoparticles are formed by solid-state dewetting on epitaxial GaN film grown by molecular beam epitaxy (MBE). The morphology of epitaxial GaN layers, thin Au and Au films, and a distributed array of nanoparticles has been studied.
The theoretical and experimental optical characteristics show the appearance of the surface plasmon resonance effect. The results of the work show the possibility of increasing the efficiency of GaN-based optoelectronic devices.

Figure 6. Transmission and reflection spectra of Au/GaN/c-Al₂O₃(a) and Au/GaN/c-Al₂O₃(b) samples after high-temperature annealing.

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