Profiles of ion-doped layers on gallium arsenide

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Abstract. We studied the concentration profiles of charge carriers that are characteristic for ion-doped layers (IDL) used in the manufacturing of field-effect transistors with a Schottky barrier (FTS) on gallium arsenide. Silicon was used as a dopant in the formation of n- and n⁺-n layers on GaAs. During annealing of the IDL, SiO₂ films were used as protective coatings. The impurity content and silicon distribution in the IDL were estimated by the SIMS method. Profiles of ion-doped layers were calculated by the LSB method. The method for measuring of surface concentration consists in the constant chemical etching of thin layers of gallium arsenide and the measurement of surface electrophysical characteristics. The experimental concentration profiles for GaAs are not Gaussian, but have wide “tails” due to channeling effects in crystals and the influence of chromium. The modes of ion implantation are considered, which form IDL with a sharper profile of the concentration of charge carriers in the “tail”.

1. Introduction

Microwave transistors based on gallium arsenide are widely used due to the features such as high gain coefficient, high linearity of amplitude characteristics, high reliability, long-term stability, and developed technology of manufacturing.

Arsenide-gallium field effect transistors with Schottky gate (FTS) are widely used in various fields, such as cellphone industry, high-speed fiber-optic communications, wireless data transmission, satellite communications and radiodetection and ranging. Structures for the manufacture of these transistors are formed in two ways: by the method of epitaxial growth of active layers on a semi-insulating substrate and by the method of ion implantation in the substrate. Epitaxial FTS are characterized by higher parameters in the microwave range, while ion-doped ones are characterized by comparative simplicity of manufacture [1, 2]. When developing powerful solid-state microwave amplifiers using ion implantation (II), n⁺-doped layers are created [3].

The use of ion implantation in the technology of manufacturing of GaAs field-effect transistors is based on the advantages of this method: high uniformity of doping, reproducibility of processes, isotopic purity and accuracy of dosing of dopants, the possibility of forming of local and different-doped regions, controlling of the concentration profile, creating of insulating regions by proton bombardment.

The characteristics of an ion-doped transistor (saturation current, threshold voltage, breakdown voltage, and slope of the transfer characteristic) depend on the parameters of the substrate, namely, the concentration of deep and shallow impurities, and also on the parameters of the doping profile: the position of the peak concentration of the doping impurity, the width of the doping profile, the concentration of the doping impurity at the maximum of the profile, which is formed by implantation of silicon ions in a substrate [4].
With a decrease in the width of the doping profile, both the power of the transistor and its gain increase simultaneously; therefore, in the manufacture of ion-doped structures, one should strive to obtain the narrowest and sharpest profile [5].

Relatively small mass of silicon ions (Si\textsuperscript{28}+), less criticality, compared with group VI impurities of the periodic table to the type of protective coating during annealing, high degree of activation of Si\textsuperscript{+} ions implanted, the possibility of ion implantation without heating the substrates determined the choice of silicon as a dopant during the formation of n- and n\textsuperscript{−} layers on GaAs. A disadvantage of silicon as a dopant is that, along with Si\textsuperscript{+} ions, N\textsubscript{2} and CO\textsuperscript{−} ions of equal mass can be introduced into the substrate, as well [6, 7].

2. Protective coatings for annealing of ion-doped layers

One of the problems of ion implantation in GaAs is the surface dissociation of the sample at commonly used annealing temperatures from 700 to 900°C. To prevent this phenomenon, protective coatings are used: Si\textsubscript{3}N\textsubscript{4}, SiO\textsubscript{2}, AlN, layers of semiconductor materials, etc. [8]. Annealing of IDL without surface protection is also widely used.

One of the methods for annealing of ion-doped GaAs layers is the powder method, which allows creating of excess pressure of arsenic vapors and thereby preventing dissociation of the GaAs surface. The second option for annealing IDL on GaAs is the use of SiO\textsubscript{2} films as protective coatings. For GaAs samples implanted with Si\textsuperscript{+} ions, unlike other impurities, the degree of electrical activation increases when using a SiO\textsubscript{2} protective coating. The dependence of the activation degree on the protective coating material is explained by the difference in the concentration of Ga and As at the GaAs interface with the dielectric.

SiO\textsubscript{2} films with thickness of 0.2 microns on semi insulating gallium arsenide are applied by oxidation of monosilane with oxygen at a pyrolytic deposition unit O2MS–500–003–SCHTS M3.020.003 for low temperature dielectric films. To obtain high-quality dense layers on the surface of GaAs substrates, it is necessary to maintain a heterogeneous reaction at temperatures of 300 –450 °C, which provides desorption of water molecules from the resulting film.

Annealing of the GaAs IDL in the presence of a SiO\textsubscript{2} protective coating leads to a significant redistribution of chromium in the near-surface layer of GaAs. The concentration of chromium after annealing increases sharply, by several orders of magnitude, at the edge with SiO\textsubscript{2}. One of the most important reasons for this redistribution of chromium is the presence of mechanical stresses at the GaAs–SiO\textsubscript{2} interface. In addition to the stressed GaAs–SiO\textsubscript{2} interface, the nature of chromium redistribution is influenced by gettering of the defects in the implanted layer.

Besides the effect of chromium redistribution in the substrate during annealing of GaAs-SiO\textsubscript{2} systems, another characteristic feature of annealing is the diffusion of gallium in SiO\textsubscript{2}.

Thus, in the case of annealing of ion-doped GaAs layers in the presence of SiO\textsubscript{2} protective coatings, GaAs interacts with SiO\textsubscript{2} by following way: gallium diffuses in SiO\textsubscript{2} and chromium redistribution occurs near the surface. A significant disadvantage of Si\textsubscript{3}N\textsubscript{4} films is their cracking and peeling during high-temperature annealing due to the difference of almost 2 times the thermal coefficients of linear expansion of gallium arsenide and Si\textsubscript{3}N\textsubscript{4} films. Therefore, the use of SiO\textsubscript{2} and Si\textsubscript{3}N\textsubscript{4} as protective dielectric coatings can lead to a dispersion of the parameters of ion-doped layers. Of interest is the use of native gallium arsenide oxides for the formation of ion-doped GaAs layers with increased uniformity of characteristics. As protective coatings, along with SiO\textsubscript{2} films, two-layer coatings are used: native-grown oxide-SiO\textsubscript{2}, native-grown oxide-Si\textsubscript{3}N\textsubscript{4}.

Oxide films obtained by thermal and pulsed thermal oxidation are used as native-grown oxides. Ion-doped GaAs layers are formed by ion implantation of silicon through GaAs native-grown oxide films, followed by their use in the annealing of the ion-doped layer.

The use of native-grown oxides in the technology of forming of ion-doped layers, along with increasing the uniformity of their characteristics, allows reducing the level of carbon – containing compounds on the surface, reducing mechanical stresses at the GaAs-dielectric interface and,
consequently, the redistribution of chromium to the surface and reducing the efficiency of decomposition of gallium arsenide.

3. Evaluation of impurity composition of gallium arsenide
Table 1 shows the results of the analysis of chromium content in semi-insulating gallium arsenide. As follows from the table 1, there is a good agreement for various methods for determining of the chromium content in semi-insulating gallium arsenide and it is reasonable to determine the concentration of chromium in GaAs by optical method. For other impurities, shallow donors Si, S, and transition metal Fe (less important in practical sense), the impurity concentrations determined by the SIMS method are lower than those determined by laser mass spectrometry. High concentrations of carbon (8.8×10^{16}, 5.7×10^{17} cm^{-3}) according to laser mass spectrometry can be associated with the adsorption of carbon on structural breakings in the GaAs layer enriched with arsenic, with a low content of gallium and oxygen.

Taking into account the important role of chromium in the phenomenon of thermal conversion and its significant influence on the Hall mobility, it is of practical interest to analyze the distributions of electron concentrations during the implantation of silicon ions for semi-insulating GaAs substrates with different mobility of charge carriers.

### Table 1. Results of analysis of the impurity content in semi-insulating gallium arsenide.

| Boule grade | Method of analysis | Concentration of impurities, cm^{-3} | Cr | Si | S | Fe |
|-------------|--------------------|-------------------------------------|----|----|---|----|
| AGCHP–6 (CH–263) | SIMS Optical absorption | 4.5×10^{15}–1.4×10^{16} | (1.2–1.4)×10^{16} | (1.0–2.4)×10^{15} | <10^{15} |
| AGCHP–6 (CH–263) | Laser mass spectrometry | 6×10^{15}–1×10^{16} | – | – | – |
| AGCHP–2a (CH–75) | SIMS Optical absorption | 8.8×10^{15}–1.3×10^{16} | (2.4–4.6)×10^{16} | 8.0×10^{15} | (1.8–3.7)×10^{16} |
| AGCHP–2a (CH–75) | Laser mass spectrometry | 2.1×10^{16}–3.1×10^{16} | (1.3–1.6)×10^{16} | (2.3–2.7)×10^{15} | (1.4–1.8)×10^{15} |
| AGCHP–2a (CH–75) | Laser mass spectrometry | 2.5×10^{16}–5×10^{16} | – | – | – |
| AGCHP–2a (CH–75) | Laser mass spectrometry | 6.6×10^{15}–4×10^{16} | (1.5–5.7)×10^{16} | 8.8×10^{15} | (1.1–1.5)×10^{16} |

4. Profiles of electron concentrations during implantation of silicon ions in gallium arsenide
The penetration depth of the embedded impurity and its spatial distribution are given by the path theory or the Lindhard-Scharf-Schiott (LSS) theory [9, 10]. The authors of the LSS theory considered the spatial distribution of embedded ions using mathematical statistics. The exact result of this consideration is not expressed in elementary functions, but can be approximated by the following expression, called the Pearson distribution:

\[ N(x) = \frac{2K_{act}\phi}{\sqrt{2\pi \Delta R_p}} \left(1 + \text{erf}\left(\frac{R_p}{\sqrt{2}\Delta R_p}\right)\right) \exp\left[-\frac{(x - R_p)^2}{2\Delta R_p^2}\right], \]

where \( \phi \) is the dose of embedded ions; \( R_p \) is the average projected path; \( \Delta R_p \) is the dispersion of projected paths; \( \text{erf} \) ( ... ) is the error function; \( x \) is the coordinate in the direction of the initial movement of the ion beam (the reference point is on the target surface); \( K_{act} \) is the impurity activation coefficient.

The value \( K_{act}\phi/\sqrt{2\pi \Delta R_p} \) gives the concentration of the doping impurity in the maximum of profile. The activation coefficient is equal to the ratio of the concentration of an electrically active impurity after the annealing process to the total concentration of the implanted impurity. When Si^{+} ions were implanted in GaAs, the values of \( R_p \) and \( \Delta R_p \) were determined from [11].

The position of the concentration peak of the dopant was determined relative to the surface of the transistor, on which the source, drain and gate electrodes are located. The parameters of the doping profile are determined by the parameters of ion implantation process: implantation energy, ion dose of
implanted impurities, the thickness of the dielectric film through which implantation was conducted, temperature and time of activation annealing. Changing one of the technological parameters of the implantation process leads to a change in all the parameters of the doping profile at once.

For practical purposes, especially when the $<R_p>$ is a few tenths of a micrometer or less, a simpler Gauss distribution is more often used:

$$N(x) = \frac{K_{\text{acc}}\phi}{\sqrt{2\pi}\Delta R_p} e^{\exp\left[-\frac{(x - R_p)^2}{2\Delta R_p^2}\right]}$$

Figures 1 and 2 show the electron concentration distributions obtained from C-V measurements and the calculated distributions of embedded silicon atoms (E = 125 keV, annealing under SiO$_2$ film at 850°C, 20 minutes in N$_2$ + H$_2$) in GaAs (AGCHP–1 grade) for various initial mobility in a semi-insulating substrate.

The concentration of chromium in the studied GaAs samples of the AGCHP–1 grade was $2.5 \times 10^{15} - 2 \times 10^{16}$ cm$^{-3}$ according to various methods. The difference between experimental and calculated distributions of electron concentration in the $\approx R_p$ region may be due to the compensating effect of chromium and its redistribution during annealing of implanted layers. The greatest difference between experimental and calculated distributions is observed for samples with a low electron mobility of 1000 cm$^2$/V×s and the highest concentration of chromium.

**Figure 1.** Comparison of electron concentration profiles obtained from C-V measurements with the data obtained during implantation of silicon ions in gallium arsenide: E = 125 keV; annealing under SiO$_2$, $T_{\text{ann}}$=850 °C; semi-insulating GaAs (AGCHP–1), $\mu$ = 3500 cm$^2$/V×s; 1, 2, 3, 4 – experiment; 5, 6, 7, 8 – calculation (LSS).

**Figure 2.** Comparison of electron concentration profiles obtained from C-V measurements with the data obtained during implantation of silicon ions in gallium arsenide: E = 125 keV; annealing under SiO$_2$, $T_{\text{ann}}$=850 °C; semi-insulating GaAs, (AGCHP–1), $\mu$ = 1000 cm$^2$/V×s; 1, 2, 3, 4 – experiment; 5, 6, 7, 8 – calculation (LSS).

5. Calculated and experimental profiles of charge carriers and silicon ions concentration

Figure 3 shows the results of measurements of the layer concentration $n_S$ during the layer-by-layer chemical etching of GaAs implanted with Si$^+$ ions. The sharpest distribution of charge carrier concentrations is typical for samples of semi-insulating GaAs with high electron mobility of 3500 cm$^2$/V×s and 5200 cm$^2$/V×s. The extended “tail” of the carrier concentration distribution is particularly undesirable for FTS channels where the cutoff voltage of the Vgic is required to be controlled, since the contribution
of “false” donors to the Vgic becomes more significant at greater depths. The appearance of a deep “tail” is strongly associated with the conversion of the n-type surface in non-implanted samples, which, in turn, is associated with the concentration of chromium in the boule.

![Figure 3](image_url)

**Figure 3.** $n_s$ changes vs depth of ion-doped gallium arsenide layers during layer-by-layer chemical etching: implantation modes of Si$^{+}$ ions; $E = 125$ keV, $D = 5 \times 10^{12}$ cm$^{-2}$.

Implanted n-i and n'-n-i-type structures were used for the manufacture of FTS. To create a sharper distribution of the implanted silicon, implantation of ions was performed at an angle of 5–6° to the normal relative to the sample surface with (100) orientation [12]. The concentration profiles of charge carriers typical for the IDL used in the manufacture of FTS are shown in figure 4. At the implantation dose of $1 \times 10^{13}$ cm$^{-2}$ and the energy of the implanted Si$^{28}$ ions 125 keV (n-i-structure), the maximum concentration of charge carriers in the active layer is $\approx 2.5 \times 10^{17}$ cm$^{-3}$ (curve 2), and at the dose of $2.5 \times 10^{13}$ cm$^{-2}$ and $E = 50$ keV (n'-layer), the concentration is $\approx 10^{18}$ cm$^{-3}$ (curve 1). In the single-stage doping mode (curve 2), an n – layer with a depth of $\approx 0.20$ μm is formed, and in the two-stage mode, an n' -layer with a maximum concentration of electrons in the layer $\approx 10^{18}$ cm$^{-3}$ and a depth of $\approx 0.25$ μm (curve 3).

Figure 5 shows the distribution of charge carrier mobility over the depth of the IDL. The mobility of charge carriers in the IDL increases in the direction of the interface IDL -substrate. The further decrease in mobility is probably due to the influence on the measurements of the transition layer at the interface IDL -semi-insulating substrate. The decrease in mobility near the substrate surface is probably due to the accumulation of chromium near the surface during thermal annealing. This effect is partially eliminated by subetching of the IDL in a slow etcher. Of practical interest is the increase in the mobility of charge carriers in the direction of the n-i interface, near which the transfer of charge carriers occurs in the normal mode of FTS operation.

The experimental profile of the concentration of implanted silicon ions, measured by the SIMS method, and the calculated profile of “Pearson-IV” are shown in figure 6. In contrast to LSS calculations, experimental profiles for GaAs are not Gaussian, but have wide “tails” due to channeling effects in crystals. Implantation profiles significantly affect the electrical characteristics of the FTS. At low displacements on the gate, the steepness of devices with profiles of the distribution of silicon atoms obtained during implantation is less than that of FTS with rectangular profiles.
Figure 4. Distribution of charge carrier concentrations in various ion $^{28}$Si implantation modes: a) experimental distributions, b) comparison of the calculated distribution with experimental ones.

Figure 5. Distribution of the Hall mobility of charge carriers over the depth of ion-doped layers of gallium arsenide: Si$^+$ implantation; powder annealing method at $T_{\text{ann}} = 750^\circ\text{C}$, $t = 30$ minutes.

Figure 6. Experimental and calculated profiles of the concentrations of implanted silicon ions in gallium arsenide: $E = 150$ keV, $D = 4.5 \times 10^{12}$ cm$^{-2}$.

6. Control of the “tails” of concentration profiles of charge carriers
The steepness at low displacements can be increased by introducing acceptor impurities into the substrate or by forming a buried p-layer. Deep implantation of small doses of $^{24}$Mg$^+$ acceptors together with the main donor impurity allows compensating the “tail” part of the electron distribution. However,
the introduction of $^{24}\text{Mg}^+$ ions requires high energy, so the technology of introducing dual-charge (lighter) $^{16}\text{O}^+$ ions is considered as more effective.

The modes of joint ion implantation of silicon and oxygen and the parameters of gallium arsenide IDL for different annealing temperatures are shown in table 2, the calculated distributions of concentrations of silicon and oxygen atoms are shown in figure 7.

As follows from table 2, when $\text{Si}^+$ and $\text{O}^{++}$ are implanted together, the annealing temperature of the implanted layers is higher (900°C) compared to the “single” $\text{Si}^+$ implantation mode (850°C), which may be associated with additional defect formation during joint implantation.

| Table 2. Parameters of ion-doped gallium arsenide layers during joint implantation of silicon and oxygen. |
|---|---|---|---|---|
| The grade of original substrate | The modes of implantation | The annealing conditions | IDL parameters |
| | $E_1$, keV | $D_1$, cm$^2$ | $E_2$, keV | $D_2$, cm$^2$ | $T_{ann}$, °C | $t_{ann}$, min | $\mu_s$, cm$^2$/V×s | $n_s$, cm$^2$ | $R_s$, Ω/□ |
| AGChP–2 (CH–779) | 100 | $4\times10^{12}$ | 150 | $6.3\times10^{12}$ | 700 | 20 | – | – | 1216 |
| | 750 | 20 | 3100 | $1.7\times10^{12}$ | 872 |
| | 800 | 20 | 3200 | $2.3\times10^{12}$ | 872 |
| | 850 | 20 | 3500 | $4.6\times10^{12}$ | – |
| | 900 | 10 | 3330 | $4.8\times10^{12}$ | 403 |
| AGChP–4 (CH–793) | 100 | $4\times10^{12}$ | 150 | $6.3\times10^{12}$ | 700 | 20 | – | – | 1975 |
| | 750 | 20 | 2060 | $1.6\times10^{12}$ | – |

Figure 7 shows the surface concentration distributions obtained by layer-by-layer etching of IDL for cases of joint implantation of $\text{O}^{++}$ and $\text{Si}^+$ ions. In cases of joint implantation of oxygen and silicon, there is a sharp drop in $n_s$ in the “tail”, in contrast to cases of “single” implantation of silicon ions. At the same time, the essential role of the initial semi-insulating gallium arsenide in the effects of controlling the “tails” of concentration profiles is revealed. For substrates from AGCHP–2 boule, which has a considerably smaller leakage currents due to the presence of deep levels, effects in the “tail” are more pronounced than for substrates from AGCHP–4 boule with large leakage currents together with significant “macro-nonuniformities” over the substrate. Taking into account the modes for creation of IDL during the joint implantation of $^{16}\text{O}^{++}$ and $^{28}\text{Si}^+$ ions, the likeliest mechanism for controlling of the “tails” of the concentration profiles of charge carriers is compensation associated with the damages caused by the implantation of oxygen ions [6].

Positive results on the “tails” controlling of concentration profiles were obtained with the sequential introduction of oxygen, and then silicon. When oxygen is introduced into silicon-implanted GaAs layers, the effects of controlling of the “tails” of concentration profiles are weak. This may be due to the formation of complex clusters with residual impurities and defects when introducing oxygen into the implanted layers, for example, when replacing arsenic with oxygen. As a result, the compensating role of the imperfections introduced during the implantation of oxygen is reduced. The effects of controlling of the “tails” of concentration profiles were also observed for high doses of introduced ions: $0.75\times10^{13}$ cm$^2$ for silicon and $(1–1.6)\times10^{13}$ cm$^2$ for oxygen.

Thus, with the joint implantation of oxygen and silicon, it is possible to form layers with a sharper profile of the concentration of charge carriers in the “tail” with a depth of $\approx0.2$ μm, the concentration of charge carriers in the layer of $(2–2.5)\times10^{17}$ cm$^{-3}$, and a mobility higher than $3000$ cm$^2$/V×s. The use of joint implantation of oxygen and silicon leads to an improvement in the parameters of FTS.
Figure 7. ns changes over the depth for ion-doped gallium arsenide layers and calculated distributions of silicon and oxygen ion concentrations during joint implantation. Implantation modes: Si\(^+\) – E = 100 keV, D = 3.75 \times 10^{12} \text{cm}^{-2}; \text{O}^{++}– E = 300 \text{keV}, D = 6.25 \times 10^{12} \text{cm}^{-2}; T_{\text{ann}} = 850\,\text{°C}.

7. Conclusion

The concentration profiles of charge carriers, that are characteristic for the IDL used in the manufacture of field-effect transistors with a Schottky barrier on gallium arsenide, have been studied. The relatively small mass of silicon ions (Si\(^{28}\)), lower criticality in comparison with the impurities of group VI of the periodic table to the type of protective coating during annealing, a high degree of activation of embedded Si\(^+\) ions, and the possibility of ion implantation without heating the substrates determine the choice of silicon as an doping impurity in the formation of n - and n'-n-layers on GaAs. It is advisable to use silicon dioxide films as protective coatings during the annealing of IDL. A method for measuring of surface concentration based on chemical etching of thin layers and measurement of surface electrophysical characteristics is proposed. The experimental concentration profiles measured by layer-by-layer etching and SIMS methods are not Gaussian for GaAs, but have wide “tails” due to channeling effects in crystals and the influence of chromium. We have considered ion implantation modes that form an IDL with a sharper profile of the concentration of charge carriers in the “tail”. In cases of joint implantation of oxygen and silicon, there is a sharp drop in n\(_S\) in the “tail”, in contrast to cases of “single” introduction of silicon ions. When reducing the width of the doping profile, both the power of the transistor and its gain increase simultaneously, therefore, in the process of manufacture of ion-doped structures, it is necessary to strive to obtain the narrowest and sharpest profile.

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