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Effect of Si^+ ion irradiation of α-Ga_2O_3 epitaxial layers on their hydrogen sensitivity

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Abstract. The effect of Si^+ ion irradiation of α-Ga_2O_3 at doses of $8\cdot10^{12}$ cm^{-2}, $8\cdot10^{14}$ cm^{-2}, and energy of 100 keV on the gas-sensitive properties has been studied. It is shown that irradiation of α-Ga_2O_3 layer grown by halide vapor phase epitaxy with implanted Si^+ ions allows effective control of its sensitivity to H_2, response, and recovery times, as well as varying the operating temperatures. The maximum sensitivity to H_2 occurred for samples with Si^+ ion irradiation dose of $8\cdot10^{12}$ cm^{-2} at 400ºC. The mechanism of sensitivity of α-Ga_2O_3 epitaxial layers irradiated with Si^+ to H_2 is discussed.
Keywords: α-Ga_2O_3, halide vapor phase epitaxy, ion implantation, gas sensitivity

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1. Introduction

Gallium oxide with a corundum-like structure (α-Ga_2O_3) is a promising ultra-wide bandgap semiconductor. It is of interest for the development of both power diodes, field-effect transistors (FETs) [1] and solar-blind photodetectors, gas sensors [2,3]. The sensitivity of epitaxial layers of metastable α- and ε(κ)-Ga_2O_3 to gases, including H_2, depends largely on the donor's concentration (N_d) [4]. Sn [5,6] and Si [7-10] are known to be used as donor impurities in this case. The atomic radii of Ga and Si differ by only 3.6 % [7], which provides a better embedding of Si atoms into the α-Ga_2O_3 lattice. The electron mobility (μ_n) of α-Ga_2O_3:Si is higher than μ_n (α-Ga_2O_3:Sn) [11]. Besides, the α-Ga_2O_3 phase doped with Si, contrary to one doped with Sn, demonstrates stable electrophysical characteristics at high temperatures up to 500°C [7]. The method of donor introduction into Ga_2O_3, which provides

fine control of N_d and allows localized area handling, is ion implantation [10]. This paper is focused on the study of the Si^+ implantation effect on the gas-sensitive properties of α-Ga_2O_3.

2. Materials and methods

Layers of unintentionally doped (UID) α-Ga_2O_3, 2 μm thick, were deposited on sapphire substrates by halide vapor-phase epitaxy (HVPE) at 500°C. Metallic Ga, gaseous HCl, and O_2 were used as precursors. Two modes of α-Ga_2O_3 layers irradiation with Si^+ ions at the same energy E = 100 keV with doses (*D*) $D_1 = 8 \cdot 10^{12}$ cm^{-2} and $D_2 = 8 \cdot 10^{14}$ cm^{-2} were chosen. TRIM (Transport of Ions in Matter) software was used to simulate the ion implantation process in α-Ga_2O_3 layers. Initial and irradiated plates were used to fabricate 2×1 mm^2 samples. After that Pt contacts were deposited on their surface, resulting in the formation of planar metal-semiconductor-metal (MSM) structures on a sapphire substrate.

Rapid thermal annealing (RTA) was applied to stabilize the conductive properties of the samples, in the mode: 30 s at T = 400°C in a stream of pure dry air. Measurements of current-voltage characteristics (I-V characteristics) and time dependences of the samples' current were carried out in dark conditions and in a sealed microprobe chamber equipped with an objective table with a heater. A mixture of pure dry air, obtained by an appropriate generator, and H_2, in which the gas concentration was set using a gas mixture generator, was passed through the chamber.

3. Results and discussion

TRIM calculations showed that the maximum values of Si^+ concentration in α-Ga_2O_3 layers for D_1 is $9 \cdot 10^{17}$ cm^{-3} and for D_2 is $9 \cdot 10^{19}$ cm^{-3} corresponding to a depth (*d*) of 75 nm. The concentration of defects caused by Si^+ irradiation of α-Ga_2O_3 layers exceeds the concentration of impurity atoms by 3 orders of magnitude. The defects are concentrated mainly in the subsurface α-Ga_2O_3 layer, i.e., at $d \leq 75$ nm.

The current (*I*) in the studied structures at D = 0 (D_0) and D_1 increases exponentially with temperature. When the dose increases up to D_2, the current of the samples weakly depends on temperature (*T*). At $T \leq 200$°C I practically does not depend on D, and in high temperatures the range T = 250 – 400°C it drops with D exponentially. The I-V characteristics of the samples at D_0 and D_1 in the voltage (*U*) range U = 0-50 V are approximated by the power law: $I \propto U^l$. l decreases from 1.20±0.02 to 1.00±0.02 with increasing T from 25°C to 250°C and 350°C for D_0 and D_1 respectively and remains constant as T increases further. When the dose rises up to D_2, l = 1.5±0.1 in the range T = 200-400°C.

Exposure of the samples to H_2 leads to a reversible increase in I. Figure 1 shows the temperature dependences of the response (*S*) of α-Ga_2O_3 samples to 3 vol.% H_2 at different D. The ratio I_g/I_0 was taken as the response to H_2, where I_g is the current value of samples in a gas mixture of pure dry air + H_2; I_0 is the current value of samples in pure dry air. The samples at D_0 exhibited a weak response to H_2 in the range T = 100-400°C. A significant increase in response to H_2 occurred for the samples at D_1. However, the response of these samples could be registered in the range T = 200-400°C only. For these samples at 400ºC, the response to 3 vol. % H_2 reached 69.3 a.u. As the dose increased up to D_2, the response of the samples dropped but was evident over the entire range T = 25-400°C.

To evaluate the response rates of α-Ga_2O_3 samples being exposed to H_2, the response times t_{res} and recovery times t_{rec} were determined. They were chosen as the periods necessary to reach the level of $0.9 \times I_g$ after H_2 was supplied into the chamber and to reach the level of $1.1 \times I_0$ after the start of pumping pure air through the measuring chamber, respectively.

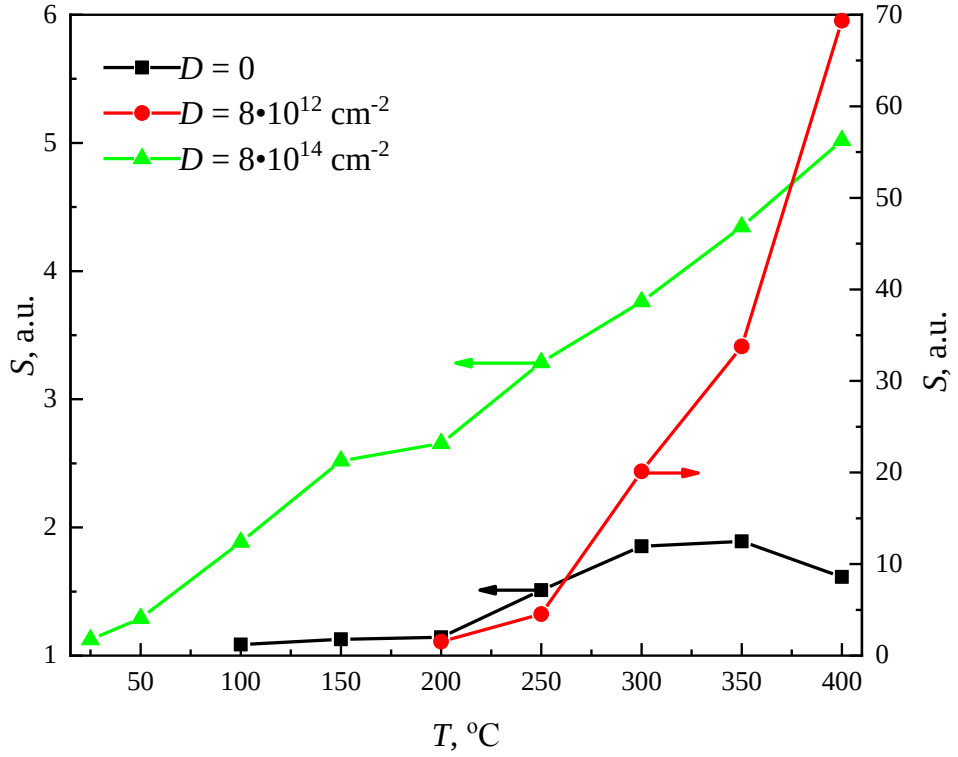

Fig. 1. Temperature dependences of the response (*S*) of α-Ga_2O_3 samples exposed to 3 vol.% H_2 at different Si^+ irradiation doses.

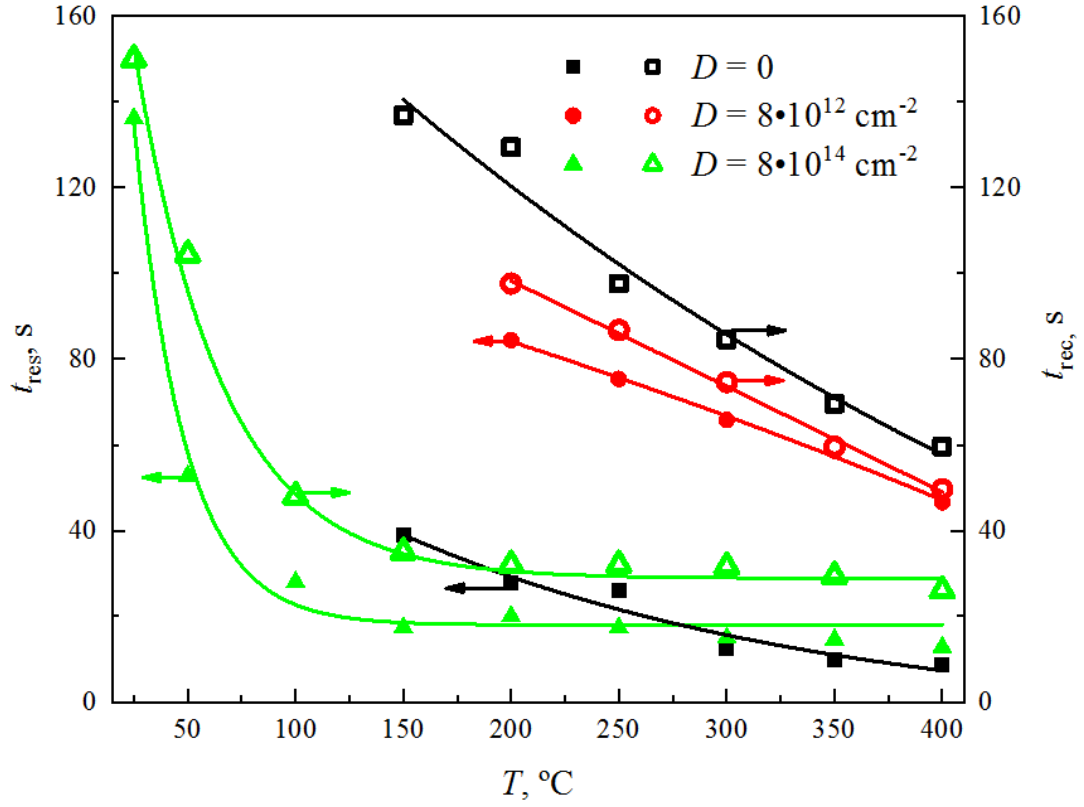

Fig. 2. Temperature dependences of the response (t_{res}) and recovery (t_{rec}) times of α-Ga_2O_3 samples exposed to 3 vol.% H_2 at different Si^+ irradiation doses

Figure 2 compares the temperature dependences of t_{res} and t_{rec} for α-Ga_2O_3 samples at D_0, D_1, and D_2. For all these curves t_{res} and t_{rec} decrease exponentially with increasing in T. The α-Ga_2O_3 samples with the highest response to H_2, at D_1 demonstrate the largest t_{res}. At $T \geq 300$°C, at D_0 and D_2, in both cases, t_{res} do not exceed 25 s. Unirradiated α-Ga_2O_3 samples are characterized by the highest t_{rec} values.

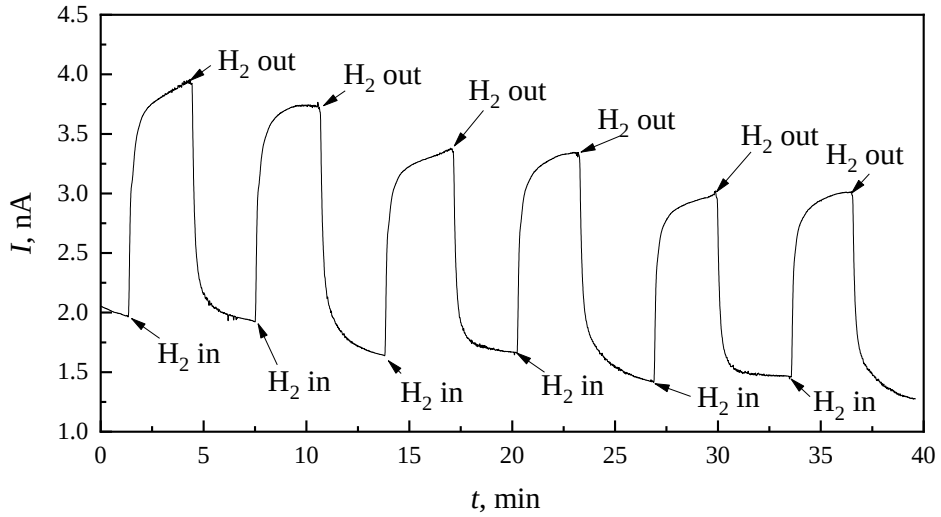

Fig. 3. Time dependence of the current (I) of α-Ga_2O_3 sample after Si^+ irradiation with $D = 8 \cdot 10^{14}$ cm^{-2} at six-fold exposer to 0.5 vol.% H_2 and $T = 400$ ℃

Time dependence of the current of α-Ga_2O_3 sample at D_2 at six-fold exposure to 0.5 vol. % H_2 and T = 400°C is depicted in Fig. 3. For these samples, I_0 decreased by 26.3 % and I_g decreased by 23.7 % after the sixth H_2 feed into the chamber. Due to the difference in the rate of decrease of I_0 and I_g over time, S increases by 1.07 a.u. For α-Ga_2O_3 samples at D_1, the opposite effects of current change with time were observed. After the sixth H_2 feed, I_0 increased by 21.9 % and I_g increased by 139.8 % compared to the first feed. Such a significant increase in I_g led to an increase in S by 2.03 a.u.

The gas sensitivity of β-Ga_2O_3 structures can be described by two mechanisms [12]. The first one is realized by chemisorption of gas molecules on the semiconductor surface, resulting in the change of charge state of the surface at T = 25-900°C and/or the concentration of oxygen vacancies in the material at T = 700-1100°C. This mechanism predominates for structures with a developed surface in which the surface conductivity contribution exceeds the bulk one. This is valid for thin and porous films, and low-dimensional structures, but is also observed for single crystals at extremely high temperatures [13]. The second mechanism is based on a change in the conditions for the flow of electron current through the potential barrier at the interface of the gallium oxide and metal (gate) with catalytic activity. This mechanism is typical of relatively thick, epitaxial gallium oxide layers [14]. Such structures are sensitive to H_2 due to weak diffusion limitations for H in the metal. It is believed that during adsorption on a metal surface, H_2 molecules dissociate into H atoms, which diffuse through the metal layer to the heterogeneous interface with the semiconductor, where they form a dipole layer that reduces the height of the potential barrier for electrons.

The thickness of the Pt contacts in the considered MSM structures was ~300 nm. The estimates showed that at the temperatures applied in this study, the time required for the diffusion of H atoms through the Pt layer does not exceed 0.055 s. While for some other molecules (CO, NH_3, NO, and NO_2) and their possible fragments this time is significantly longer. A Schottky barrier is formed at the Pt / α-Ga_2O_3 interface [13]. The saturation current of such a barrier in the air is $I_{s0} = AA^*T^2\exp[-\Phi_{b0}/(kT)](kT)]$, where A is the contact

area; A^* is Richardson constant; e is electron charge; k is Boltzmann constant; Φ_{b0} is the potential barrier height at the Pt / α-Ga_2O_3 interface in an atmosphere of pure dry air. In a pure dry air + H_2 gas mixture, Φ_{b0} decreases by the value of $e\Delta V_H$ and $\Phi_{bH}(n_{H2}) = \Phi_{b0} - e\Delta V_H(n_{H2})$, where Φ_{bH} is the height of the potential barrier at the Pt / α-Ga_2O_3 interface when exposed to H_2. It is not difficult to show that $S(n_{H2}) = \exp[e\Delta V_H(n_{H2})/kT]$. As T increases from 100°C to 350°C at D_0, $e\Delta V_H$ increases from 0.003 eV to 0.034 eV.

To increase the response of α-Ga_2O_3 to H_2 an increase in ΔV_H is necessary. It is shown [14,15], that $\Delta V_H = p \times \theta_H \times N_i/\varepsilon_0$, where p is the dipole moment created by the H atom on the heterogeneous interface; θ_H is the coverage of the Pt / α-Ga_2O_3 interface by H atoms, $\theta_H \leq 1$ and $\theta_H = n_H/N_i$; n_H is the surface density of H atoms adsorbed on the interface; N_i is the surface density of adsorption centers for H on the interface; ε_0 is the dielectric constant. At T = 350°C and n_{H2} = 3 vol. % $p \approx 6.67 \cdot 10^{-30}$ C×m [15,16]. The dependences of $e\Delta V_H$ on H_2 concentration are approximated by power functions, $e\Delta V_H \sim n_{H2}{}^m$, and at n_{H2} > 1 vol. % tend to saturation, where m is the exponent, m = 0.32 at D_1. Hence, we can assume that when n_{H2} = 3 vol. % $\theta_H \rightarrow 1$. The N_i values obtained at T = 350°C were $4.54 \cdot 10^{14}$ cm^{-2}, $2.51 \cdot 10^{15}$ cm^{-2}, and $1.05 \cdot 10^{15}$ cm^{-2}, respectively, at D_0, D_1, and D_2. Irradiation of α-Ga_2O_3 with Si^+ ions leads to an increase in N_i and as a consequence the response to H_2 and other gases increases. When a dose is further increased up to D_2, the surface of α-Ga_2O_3 develops defects that decrease I and N_i. A similar mechanism of influence of ion irradiation on gas-sensitive properties was observed earlier for SnO_2 [17,18].

4. Conclusions

It was found that Si^+ ion irradiation of α-Ga_2O_3 epitaxial layers with a dose of $8 \cdot 10^{12}$ cm^{-2} and energy of 100 keV leads to a magnification from 3 to 43 times in the H_2 response of MSM Pt/α-Ga_2O_3/Pt structures with increasing the heating temperature from 250°C to 400°C. When the irradiation dose is increased up to $8 \cdot 10^{14}$ cm^{-2}, a significant decrease in the H_2 response, response, and recovery times are observed. We attribute the observed effect to an increase in the density of adsorption centers for H atoms on the Pt / α-Ga_2O_3 interface when α-Ga_2O_3 is irradiated with Si^+ ions at a dose of $8 \cdot 10^{12}$ cm^{-2}. A further increase in dose up to $8 \cdot 10^{14}$ cm^{-2} generates defects on the semiconductor surface which reduce the density of adsorption centers for H on the Pt / α-Ga_2O_3 interface.

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