

Supplementary material for : Proton Damage Effects in Double Polymorph γ/β -Ga₂O₃ Structures

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Here we present a brief description of samples converted from bulk (010) Fe doped semi-insulating crystals implanted with Ga and Si and subjected to annealing. Table IS presents the implantation parameters of the samples.

Table I. Implant parameters used in the present study.

Implants		Energy (keV)	Dose (ions/cm ²)	T_i (°C)	<i>Additional annealing</i>	<i>Additional treatment</i>	<i>Sample # in the present paper</i>
initial	⁶⁹ Ga ⁺	1700	6×10 ¹⁵	RT	none	H plasma, 330oC, 0.5h	γ-GO1
additional	²⁸ Si ⁺	300	1×10 ¹⁵	200	none	H plasma, 330oC, 0.5h	γ-GO2
		36	2×10 ¹⁴	400	600oC	H plasma, 330oC, 0.5h	γ-GO3

The samples used in this study are the ones described previously in Ref. [1S]. The treatments that they underwent are presented in Table 1S. Detailed structural characterization was performed in Ref. [2S, 3S] and included Rutherford Back Scattering (RBS) experiments, XRD θ – 2θ scans of the samples, detailed Scanning Transmission Electron Microscope (STEM) experiments. Fig. 1S taken from Ref. [1S] shows the evolution of the RBS spectra and XRD pattern evolution upon Ga and Ga+Si implantation and annealing.

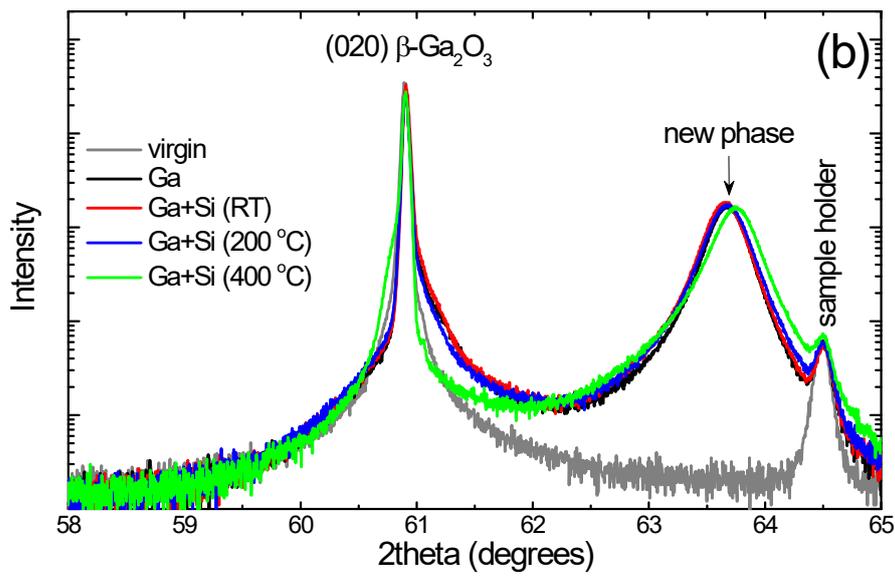
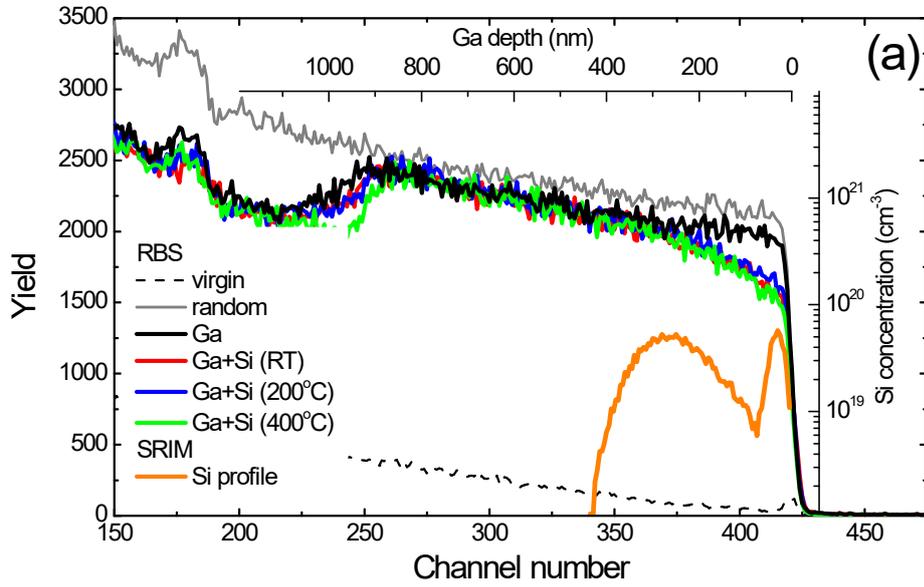


Fig. S1. (a) RBS spectra and (b) corresponding XRD Θ - 2Θ scans of the Ga_2O_3 samples co-implanted with Ga+Si ions at different temperatures as indicated in the legend. The virgin (unimplanted) RBS/C is shown for comparison.

From Fig. S1(a), Ga implantation produced a surface modified layer with thickness $\sim 1 \mu\text{m}$. The channeling yield in this layer corresponds to $\sim 90\%$ of the random level and, according to the previous results [1S-3S], this layer corresponds to the new phase of Ga_2O_3 . The phase transformation is also supported by XRD results (Fig. S1(b)) showing the new diffraction peak located at 63.7° which appears after implantation. Implantation also leads to the prominent broadening of the (020) β - Ga_2O_3 diffraction peak, indicating formation of some strain and defects in the interface region. Based on combined RBS, XRD, and STEM results, this phase has been identified as g- Ga_2O_3 defect spinel phase [1S-3S].

Additional Si implants were performed to make a box-like Si profile in the phase-modified layer and the Si concentration versus depth profile was formed within the new phase, extending to the 400 nm from the surface with peak concentration of about $5 \times 10^{19} \text{ cm}^{-3}$, according to the SRIM code [4S] simulations (see Fig. 1S(a)). These Si implants led to a decrease of the channeling yield in the near surface region, indicating some improvement of the crystalline quality in the implanted region. Furthermore, the thickness of the phase-modified layer decreased with increasing implantation temperature and its thickness became $\sim 940 \text{ nm}$ after Si implantation at 400°C (see Fig. S1(a)). Moreover, the RBS data indicate that the sharpness of the inner interface between the new and β -phases improves. According to the XRD data, the new phase still persists even after 400°C Si implantation (Fig. S1(b)) and persists after 600°C annealing. High temperature Si implantation leads to the increase of the sharpness of the (020) β - Ga_2O_3 , corroborating the RBS results.

There has been a lively discussion in the literature regarding the attribution of the new phase, but detailed analysis of STEM patterns described in detail in Ref. [2S, 3S] has persuasively demonstrated that the phase is indeed due to the defect spinel g- Ga_2O_3 forming a sharp interface with the underlying β -phase and being preserved without amorphisation even after implantation of huge doses

of various heavy ions corresponding to enormous values of displacements per atom as calculated by SRIM [4S] in Ref. [3S].

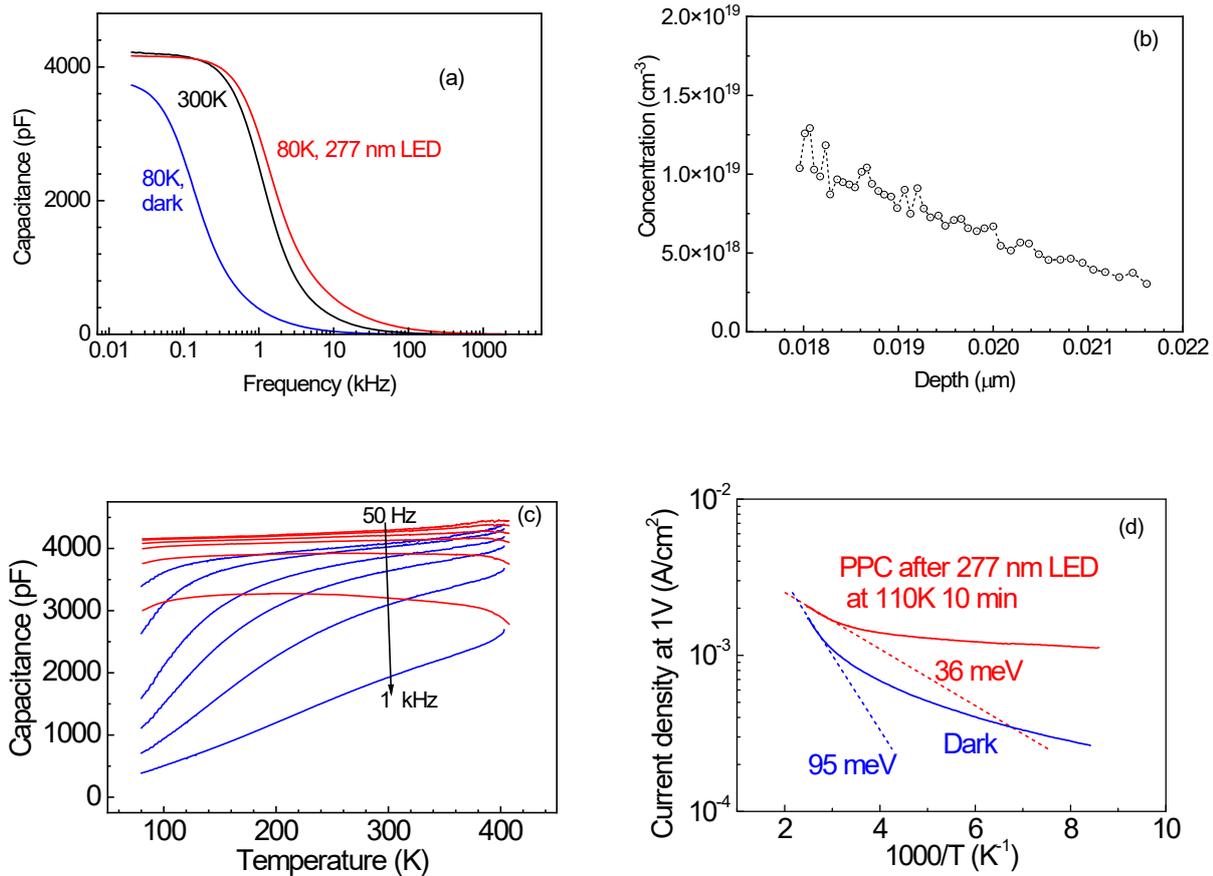


Fig. S2 (Color online) (a) C-f characteristics for sample γ -GaO1 (Ga implanted) measured at 300K, at 80K in the dark, and at 80K under illumination with 277 nm LED (the capacitance persists for a very long time after illumination); 300K concentration profile calculated from C-V measurements at 1 kHz; (c) capacitance dependences on temperature measured during cooling in the dark (blue lines) and after illumination at 80K with 277 nm LED (red lines), the data shown for frequencies of 50 Hz, 100 Hz, 200Hz, 300 Hz, 500 Hz, 1 kHz; (d) current density at 1V dependence measured while cooling in the dark and after illumination with 277 nm LED at 110K

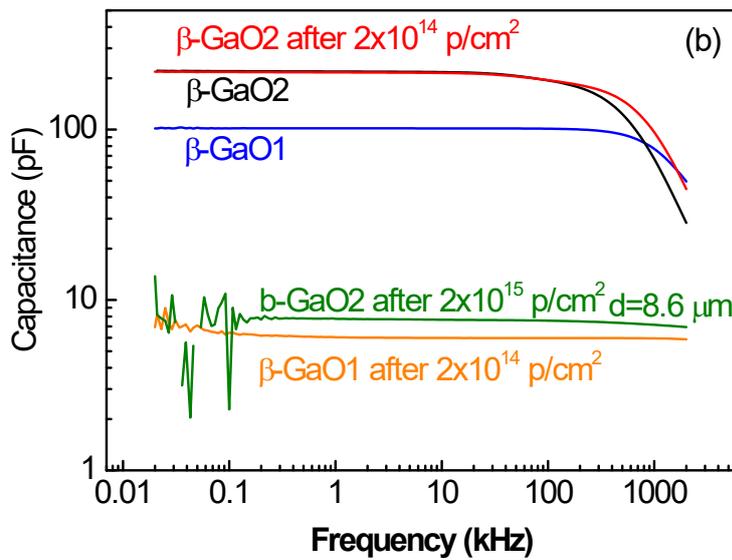
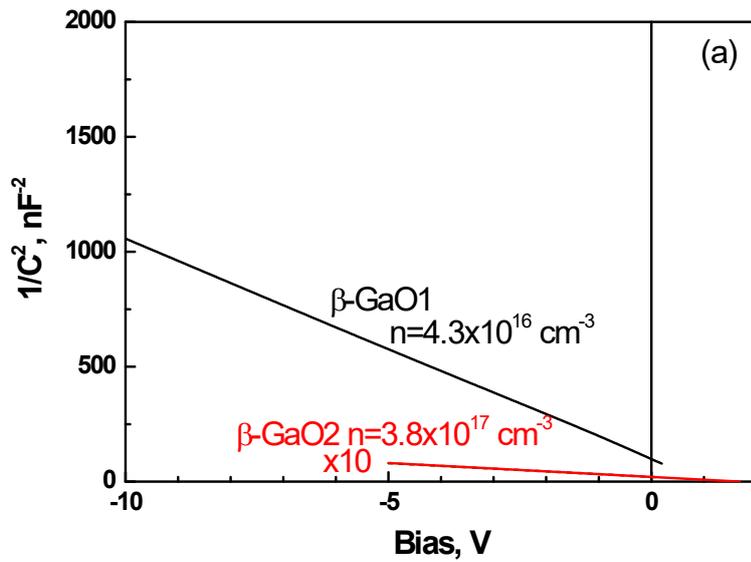


Fig. S3 (color online) (a) $1/C^2$ versus V plots for sample β -GaO1 (black line) and β -GaO2 (red line); (b) C-f characteristics for sample β -GaO1 and β -GaO2 before 1.1 MeV protons irradiation (blue line and black line respectively), after irradiation with $2 \times 10^{14} \text{ p/cm}^2$ of sample β -GaO1 (orange line) and β -GaO2 (red line) and after irradiation with $2 \times 10^{15} \text{ p/cm}^2$ 1.1 MeV protons (olive line)

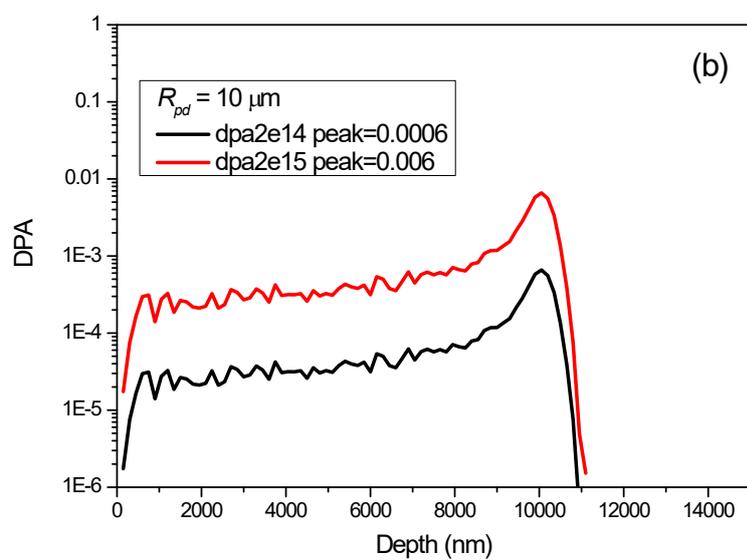
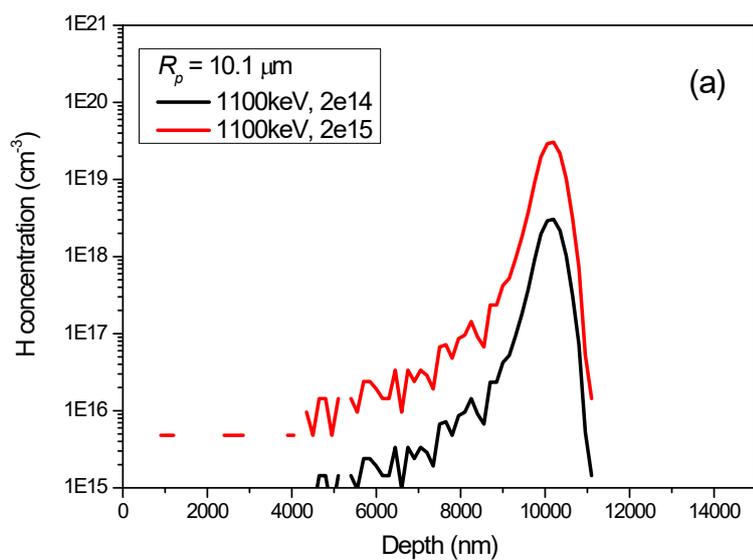


Fig. S4(Color online) (a) The distribution of H atoms implanted into Ga₂O₃ with 1.1 MeV energy and fluences of $2 \times 10^{14} \text{cm}^{-2}$ and $2 \times 10^{15} \text{cm}^{-2}$; (b) respective values of displacements per atom (DPA); calculations by SRIM [4S]

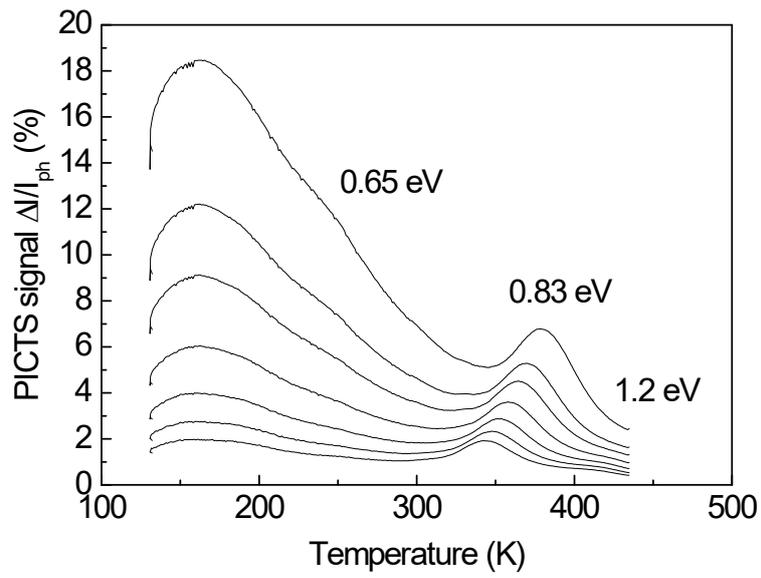


Fig. S5. PICTS spectra $\Delta I/I_{ph}$ measured for sample β -GaO1 irradiated with 2×10^{14} p/cm² 1.1 MeV protons, spectra shown for applied bias +10V on the Schottky diode, with excitation with 277 nm LED (pulse length 5 s) for time windows 150 ms/750 ms, 300 ms/1500 ms, 450 ms/2250 ms, 750 ms/3750 ms, 1200 ms/6000 ms, 1800 ms/9000 ms, and 2550 ms/12750 ms.

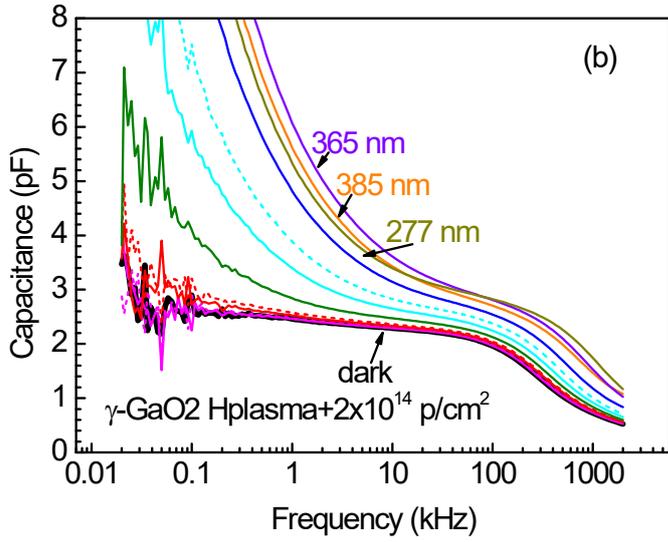
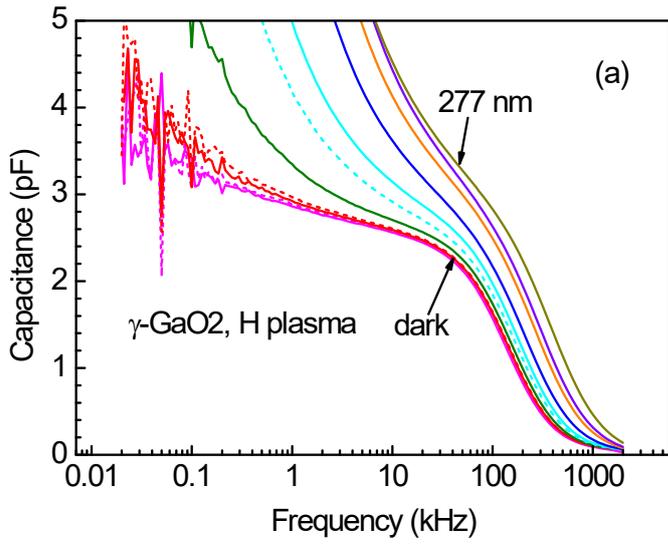


Fig. S6 (Color online) (a) C-f characteristics of sample γ -GaO₂ measured in the dark and with illumination with LEDs with peak wavelengths 940, 850, 660, 625, 530, 470, 455, 400, 385, 365, 277 nm (a) after H plasma; (b) after additional irradiation with 2×10^{14} p/cm² 1.1 MeV protons

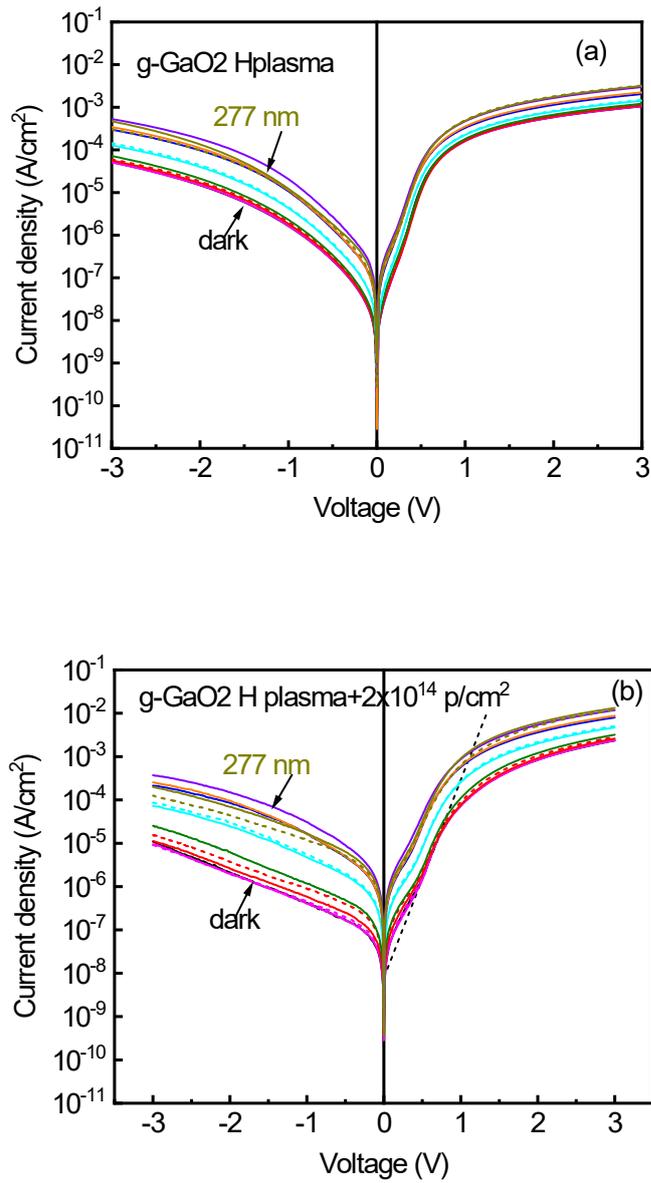


Fig. S7 (Color online) Current-voltage characteristics of sample γ -GaO₂ measured in the dark and after illumination with LEDs with peak wavelengths from 940 nm to 277 nm; measurements (a) after H plasma treatment; (b) after additional irradiation with 2×10^{14} p/cm² 1.1 MeV protons

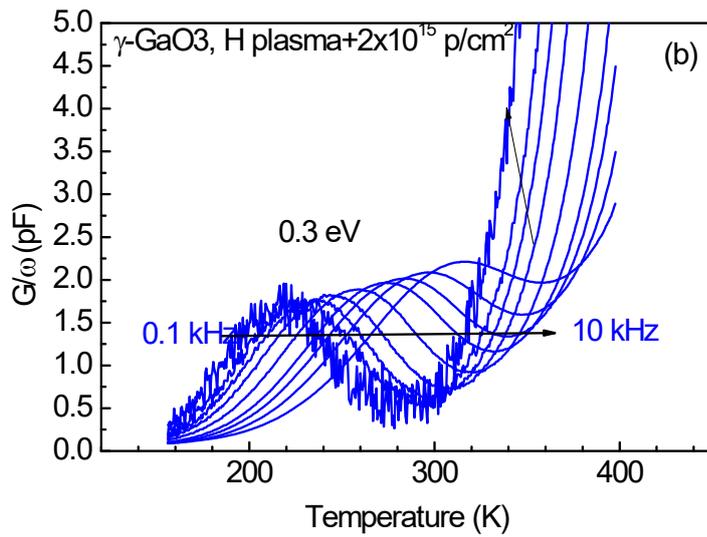
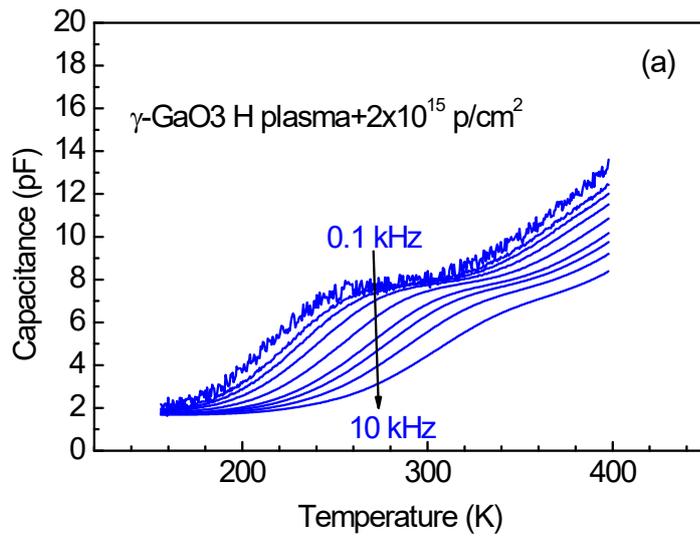


Fig. S8 (Color online) admittance spectra for sample γ -GaO₃ (a) capacitances in the 0.1 kHz-10 kHz range; (b) G/ω for the same frequencies range

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