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Photo-enhanced metal-assisted chemical etching of α -gallium oxide grown by halide vapor-phase epitaxy on a sapphire substrate and its applications†

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The development of an etching process with controllable etching rate and high selectivity is key to fabricating high-performance electronic and optoelectronic devices. In this paper, we report the photo-enhanced metal-assisted chemical (PE-MAC) etching of an ultrawide-bandgap (UWBG) alpha-phase gallium oxide (α -Ga₂O₃) semiconductor grown using a halide vapor-phase epitaxy technique. Using the PE-MAC etching process, the reproducible etch of an α -Ga₂O₃ epilayer was demonstrated at a rate of 8.24 nm min⁻¹ at room temperature; the extent of the reaction increased linearly with increasing time. The Arrhenius plot of the etching rate indicated that this process is an activation-controlled reaction with a high activation energy of 0.90 eV (86.7 kJ mol⁻¹). The Pt metal electrode, which can be removed using an acid solution, created a depletion region, making the exposed α -Ga₂O₃ epilayer etched with a smooth and tilted sidewall. The effects of the roughness at different etch temperatures were also investigated. An α -Ga₂O₃-based metal–semiconductor–metal (MSM) photodetector was fabricated by using the proposed PE-MAC etching process, and the fabricated MSM photodetector exhibited improved time-dependent photoresponse characteristics with reduced defect-related time constants, confirming that our PE-MAC etching is a damage-free fabrication process with high anisotropy and selectivity. Our study demonstrates that the PE-MAC etching is an effective wet process for manufacturing electronic and optical devices based on UWBG α -Ga₂O₃ semiconductors at room temperature without vacuum plasma equipment.

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Introduction

Alpha-phase gallium oxide (α -Ga₂O₃) is an ultrawide-bandgap (UWBG) semiconductor material with great potential for next-generation high-power electronic and deep ultra-violet (UV) photodetector devices because it has the largest energy band-gap (~ 5.3 eV) and breakdown field (9.5 MV cm⁻¹) of the five known phases of gallium oxide (Ga₂O₃) (α , β , γ , δ and ϵ).^{1–3} Owing to its ultrawide bandgap energy, α -Ga₂O₃ is not

responsive to visible and UV-A/B wavelengths but selectively reacts to light in the UV-C region, making it an ideal candidate for a solar-blind photodetector (PD).^{4,5} The high breakdown fields of α -Ga₂O₃ compared with Si and other wide-bandgap semiconductors, including GaN and SiC, allow it to resist strong electric fields applied under high-power conditions, enabling low-loss and high-voltage operation.⁶ The bandgap engineering of α -Ga₂O₃ has been investigated by alloying it with various metals (Ti, Al, Fe, Cr and In) and fabricating versatile α -Ga₂O₃-based (opto)electronic devices.⁷ Baliga's figure of merit (BFOM) is a metric to evaluate the conduction loss of a power semiconductor material and is calculated using $4V_B^2/\epsilon\mu E_g^3$, where V_B stands for the breakdown voltage, ϵ is the dielectric constant, μ is the carrier mobility and E_g is the energy bandgap.⁸ The BFOMs of α -Ga₂O₃ is 2.19 times higher than that of GaN. Furthermore, the BFOMs of α -Ga₂O₃ is 1.64 times higher than that of β -Ga₂O₃, indicating superior performance of α -Ga₂O₃ and demonstrating its potential for use in next-generation power electronics.^{9–11} The devices and the processing of β -Ga₂O₃ have been extensively studied; however, few

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† Electronic supplementary information (ESI) available: The data of PE-MAC etching are shown in Fig. S1 (32, 45, and 50 °C). Fig. S2 shows the *I*-*V* characteristics of α -Ga₂O₃ PD under dark condition as well as 254 and 365 nm lights illuminations. See DOI: <https://doi.org/10.1039/d3ma00424d>

studies have been thus far reported on the devices and processing of α -Ga₂O₃.

As semiconductor devices become increasingly integrated, the importance of controllable etching for producing finely detailed patterns is increasing. The development of a damage-free etching technology that can produce a uniform etching pattern with high anisotropy is required, allowing the manufacture of electronic and optoelectronic devices that utilize the full potential of α -Ga₂O₃.¹² The use of high-density plasma for the anisotropic etching of α -Ga₂O₃ has been investigated by using chlorine-based inductively coupled plasma (ICP) at an etch rate of 33 nm min⁻¹ with plasma power of 200 W, where a linear relationship was observed between the plasma power and etching rate.¹³ Dry etching techniques using high-density plasma offer various advantages, such as anisotropy and control of the etching rate by manipulating the plasma power. However, plasma-induced defects can degrade the device performance by increasing the leakage currents or decreasing the free-carrier concentrations.^{14,15} In contrast, wet (chemical) etching offers a vacuum-free and low-energy-consumption process compared with plasma etching and can prevent the device performance degradation due to plasma-induced damage. In addition, wet etching can be used as a cleaning process to restore the pristine surface.^{12,16} However, previously reported wet etching processes typically exhibit an isotropic etching mechanism and are not suitable for device fabrication owing to considerably low etching rates at room temperature. Choi *et al.* etched α -Ga₂O₃ using a SiO₂ etch mask in HCl solution, where the etching was achieved by reacting Ga₂O₃ with HCl to produce GaCl₃. Below the process temperature of 40 °C, the etching rate was less than 5 nm min⁻¹, suggesting very low reactivity.¹⁷ Zhang *et al.* etched β -Ga₂O₃ using phosphoric acid but did not achieve a suitable etching rate at temperatures below 140 °C (compared with a rate of 2 nm min⁻¹ at 160 °C).¹⁸ Chemical etching using an acidic solution at elevated temperatures is generally not preferred because it can generate toxic gases.

Unlike conventional wet etching, metal-assisted chemical (MAC) etching uses a metal catalyst to achieve anisotropic etching and high selectivity.¹⁹ A cathodic reaction in the metal catalyst and anodic reaction in the target material are the two key mechanisms in MAC etching. The metal removes electrons from the material to be etched and leaves holes at the interface with the material. The metal is then re-oxidized by oxidants. Subsequently, the material reacts with the holes to form ions, which makes it more reactive with the etchant. The MAC etching of Si has been reported with several metal catalysts (Au, Pd, and Pt) and hydrofluoric acid (HF) with hydrogen peroxide (H₂O₂).²⁰ Chern *et al.* produced Si nanowires with a high aspect ratio through MAC etching using Pt metal and HF.²¹ Because the accumulation of holes is an essential mechanism of MAC etching, the hole concentration is a crucial parameter to initiate and maintain the etching process. A photo-enhanced (PE) MAC etching method using UV wavelengths was developed to accumulate sufficient concentration of holes in WBG semiconductors. MAC etching involves a

catalytic reaction of the metal, and etching proceeds at the interface between the metal and the target material. In contrast, the PE-MAC etching reaction occurs in the area not in contact with the metal (irradiated by UV light).²² In addition, in the PE-MAC etching reaction, it is convenient to adjust the etching time by controlling the UV light source. The MAC and PE-MAC etching for InP substrates were demonstrated in the dark and under UV light.²³ The etchant consisted of H₂SO₄ and H₂O₂ oxidants, and the UV light for PE-MAC etching was generated by a mercury lamp (290–390 nm). In the dark, MAC etching occurred, and the InP in the region in contact with the metal was selectively etched to form a shallow groove-type structure. Conversely, upon UV irradiation, PE-MAC etching occurred, and the InP areas not covered by metal were selectively etched to form microbump arrays. In our study, PE-MAC etching was introduced to realize fast and selective anisotropic etching of α -Ga₂O₃ epilayer at low temperatures. The etching rate was calculated by varying the temperature of the etchant, and the activation energy of the reaction was estimated using the Arrhenius equation at each temperature. The electrical isolation of α -Ga₂O₃ epilayer on the insulating sapphire substrate was also achieved *via* PE-MAC etching, preceded by mesa patterning of Pt catalysts. Subsequently, the UV PD parameters were evaluated to analyze the effects of the PE-MAC etching process on the optoelectronic devices.

Experimental details

The PE-MAC etching of α -Ga₂O₃ epilayer was demonstrated using metal catalysts with high work functions and irradiation of UV-C light. Unintentionally doped α -Ga₂O₃ epilayer having a thickness of approximately 850 nm was grown on the *c*-plane sapphire substrate using the HVPE technique on a sapphire substrate. A Pt (work function: 5.65 eV) metal contact having a thickness of 20 nm was defined on α -Ga₂O₃ epilayer using a standard photolithography process (MA150e, SUSS Microtec) and electron beam (e-beam) evaporator at a rate of 0.2 Å s⁻¹, followed by a lift-off process. The pre-patterned α -Ga₂O₃ sample was annealed in a vacuum furnace (250 °C, 2 h) to enhance the adhesion of Pt with α -Ga₂O₃. High-resolution X-ray diffraction (HR-XRD; smartLab, Rigaku) was conducted to estimate crystal phases and qualities of the α -Ga₂O₃ epilayer grown on the sapphire substrate. PE-MAC etching was performed by immersing α -Ga₂O₃ in an etchant consisting of 48 wt% HF in H₂O with K₂S₂O₈ (1.5 mM) under UV irradiation (185 nm wavelength), where the light intensity of the 185 nm UV lamp was measured to be 288.6 μ W cm⁻² (FieldMax II-TO, Coherent). The etched depth was evaluated by using atomic force microscopy (AFM; NX10, Park Systems). The aforementioned procedure was repeated at various etching temperatures (22, 32, 45, and 50 °C).

A metal–semiconductor–metal (MSM) PD was fabricated to examine the optoelectrical properties of the PE-MAC-etched α -Ga₂O₃ epilayer. Mesa-patterned Pt was defined on an unintentionally doped α -Ga₂O₃ layer grown by HVPE on a sapphire



substrate to electrically isolate the active region at room temperature. The mesa-patterned Pt was removed by using aqua regia (35 °C, 30 min) solution, and interdigitated patterns were defined on the active area using e-beam lithography (MIRA3, TESCAN). Pt/Au (20/80 nm) interdigitated electrodes (IDTs) were deposited *via* e-beam evaporation to obtain the α -Ga₂O₃ MSM PD. The opto-electrical properties of the UV PD were measured using a semiconductor parameter analyzer (4155C, Agilent) connected to a low-vacuum probe station (MS TECH, 760 mmHg) under 254 nm UV irradiation (VL-6LC, Vilber Lourmat). A function generator (33250A, Agilent) and a shutter (SHB1T, Thorlabs) were utilized to control the UV irradiation time on the fabricated α -Ga₂O₃ MSM PD to obtain the time-dependent photoresponse characteristics.

Results and discussion

The mechanism of the PE-MAC etching of α -Ga₂O₃ is illustrated in Fig. 1. Fig. 1(a) shows the Pt-patterned α -Ga₂O₃ epilayer is irradiated with 185 nm UV light to generate EHPs in the surface. Then, the photogenerated electrons move to Pt with a high work function of 5.12–5.93 eV, making the holes accumulate on the surface of α -Ga₂O₃, where the holes react with gallium to generate gallium ions (Ga⁺), and gallium fluoride (GaF₃) is finally generated through the reaction between Ga⁺ and HF. Fig. 1(b) shows the re-oxidation of the Pt²⁻ that was reduced in the process shown in Fig. 1(a). The re-oxidation of Pt²⁻ reduced by accepting electrons from α -Ga₂O₃ occurs by potassium persulfate (K₂S₂O₈) in the etchant, where K₂S₂O₈ is present as peroxydisulfate (S₂O₈²⁻). S₂O₈²⁻ is decomposed into sulfate radicals (SO₄^{•-}) when irradiated with UV light of wavelength under 300 nm. Because GaF₃ was dissolved in HF, this etching process leads to the formation of a deep etched structure. If the Pt contact is unnecessary, it can be removed by using the aqua regia (35 °C, 30 min) solution. Because the metal-free area is selectively etched, this process is also called inverse-MAC etch. Fig. 1(c) shows the SEM images of α -Ga₂O₃ after PE-MAC etching. The surface of the etched region exhibits bumpy texture, which can be attributed to the disclosure of various facets of α -Ga₂O₃.²⁴ A photograph of α -Ga₂O₃ grown by HVPE on a two-inch *c*-plane sapphire substrate is shown in Fig. 2(a). HR-XRD measurements revealed that the

characteristic XRD peaks of the α -Ga₂O₃ epitaxial layer and the sapphire substrate appear at 40.12° and 41.56°, respectively, corresponding to the (0006) plane of α -Ga₂O₃ and (0006) plane of the *c*-plane sapphire in Fig. 2(b). The full width at half maximum (FWHM) of the α -Ga₂O₃ layer at 40.38° (2θ) peak slightly decreased from 209 (as-grown) arcsec to 202 arcsec (PE-MAC etched for 30 min), indicating that this process can be used to remove the defective sites. Grain size (D) can be estimated by using the following equation: $D = 0.9\lambda/[\text{FWHM} \times \cos(\theta)]$, where D of the as-grown and the PE-MAC etched α -Ga₂O₃ were 146.0 nm and 151.2 nm, respectively. The complete removal of the Pt electrodes using aqua regia was confirmed by field-emission scanning electron microscopy, as shown in Fig. 2(c). Micro-Raman spectroscopy, shown in Fig. 2(d), was performed in each area of the blue and red circles in Fig. 2(c). The Raman modes of α -Ga₂O₃ that were absent in the blue-circled area were observed in the red-circled area, indicating that the PE-MAC etching process removed the entire α -Ga₂O₃ layer until the underlying sapphire substrate, which can act as an etch-stop layer.

Fig. 3 shows the data for the PE-MAC etching of α -Ga₂O₃ in intervals of 10 min up to 60 min at room temperature (22 °C). The etch depth increased linearly with time, yielding an etching rate of 8.24 nm min⁻¹. This rate is approximately five times higher than that (2 nm min⁻¹) obtained at PE-MAC etching of β -Ga₂O₃ at room temperature, which can be attributed to the higher concentrations of the oxidants (from 0.18 (β -Ga₂O₃) to 1.5 mM (α -Ga₂O₃)) and the difference in the UV light wavelength (from 254 (β -Ga₂O₃) to 185 nm (α -Ga₂O₃)). The linearity of the extent of reaction with time and the relatively high etching rate at room temperature make the PE-MAC etching process compatible with a standard device fabrication process. The surface roughness of α -Ga₂O₃ increases linearly as etching progresses as shown in Fig. 3(b), saturating when the etching is completed at the smooth sapphire substrate. By sharp contrast, there is no correlation between the progress of etching and the surface roughness of the Pt electrode, indicating that the Pt electrode, which acts as a catalyst, does not directly participate in the etch reaction. As shown in Fig. 4(c), the Pt electrode was intact after the PE-MAC etch, implying that the underlying layer was completely protected from the etch. This is a great advantage over the conventional dry etch because the high-energy particles in the plasma etch can generate the defective sites

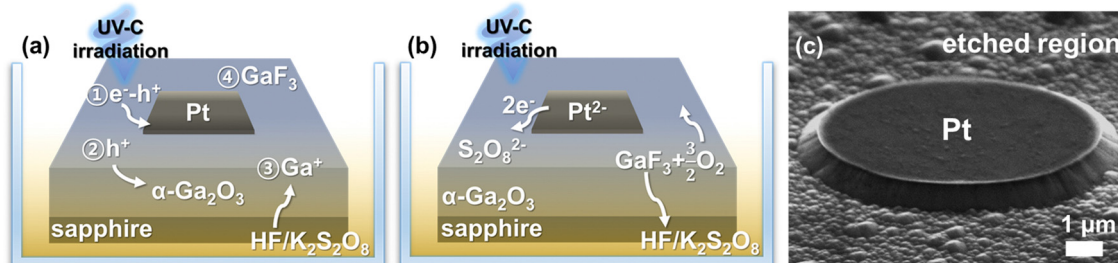


Fig. 1 Schematics of the PE-MAC etching process. (a) Formation of GaF_3 upon UV irradiation and Pt reduction. (b) Oxidation of Pt^{2-} by the oxidant ($\text{K}_2\text{S}_2\text{O}_8$) and dissolution of GaF_3 in HF. (c) Morphology of $\alpha\text{-Ga}_2\text{O}_3$ after PE-MAC etching.

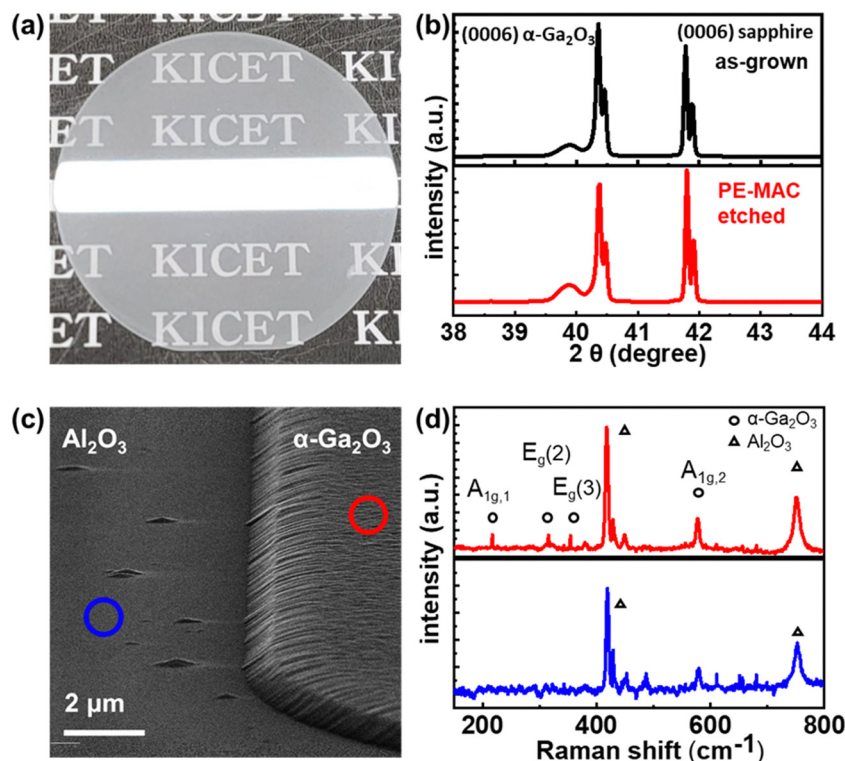


Fig. 2 (a) Photograph of the α -Ga₂O₃ epilayer on a two-inch sapphire substrate. (b) XRD patterns of the α -Ga₂O₃ epilayer on a sapphire substrate. (c) SEM image of PE-MAC-etched α -Ga₂O₃. (d) Raman spectrum of α -Ga₂O₃/sapphire (red) and sapphire (blue).

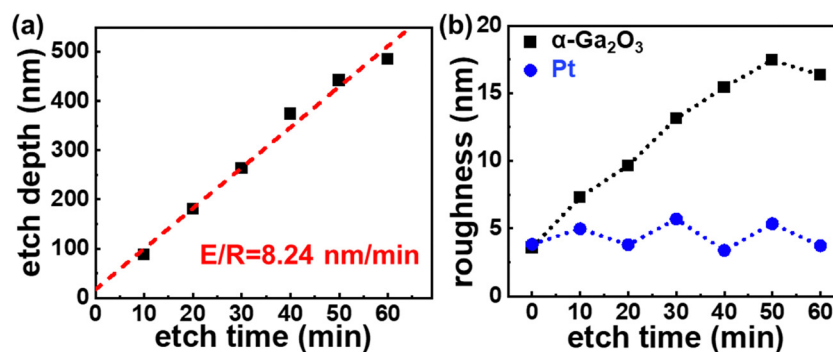


Fig. 3 (a) PE-MAC etching rate of α -Ga₂O₃ at room temperature (22 °C). (b) RMS roughness measured in a $10 \times 10 \mu\text{m}^2$ area with the progress of etching.

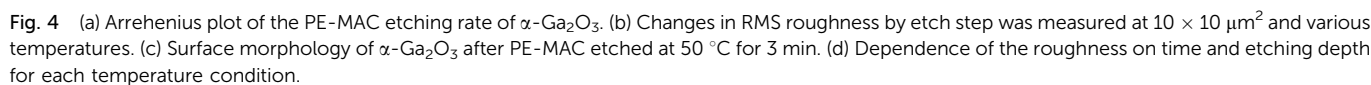
even in the photoresist-covered region owing to its incomplete coverage.²⁵ The root mean squared (RMS) roughness of the α -Ga₂O₃ surface was observed to increase by 2.8 nm per 100 nm of etching, which is similar to the roughness change observed during conventional plasma etching (ICP).¹³

Wet etching involves the (1) surface diffusion of the etchant, (2) chemical reaction between the etchant and exposed surface, and (3) removal of reaction products by etching.^{26,27} The etching reaction rate, which depends on the diffusion rate or reaction rate, can be controlled by manipulating the process parameters. At the temperature that is comparable to the effective activation energy, the diffusion rate of a substance is

slower than the rate of chemical reaction; hence, the overall reaction rate is determined by diffusion and is called a diffusion-controlled reaction. Under low-temperature conditions, the rate of the chemical reaction is slower than that of mass diffusion, and the overall reaction rate is determined by the rate of the chemical reaction that is called an activation-controlled reaction.²⁸ The temperature effect of the reaction was studied to assess the mechanism of PE-MAC etching for α -Ga₂O₃ (Fig. 4) using the following equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right), \quad (1)$$





smooth surface at high-temperature PE-MAC etch, it is necessary to optimize the process conditions that increase the number of EHPs by increasing the UV intensity, reducing the spacing of the metal catalyst, and increasing the oxidant concentration.

As shown in Fig. 4(a), a high activation energy of 0.90 eV was obtained, indicating that this reaction is activation-controlled.^{29,30} In the case of a diffusion-limited reaction, the etching species would react without being saturated on all surfaces of the target, resulting in poor reaction uniformity. Instead, the etchant is saturated on the entire surface of the target in the activation-controlled reactions, which allows a uniform reaction throughout the surface of Ga₂O₃. Fig. 4(b) demonstrates that the surface roughness increases with increasing PE-MAC etching temperature from 22 to 50 °C, where the duration of the etch process is different because of the limitation in the film thickness. The SEM image in Fig. 4(c) shows the growth domain in the α -Ga₂O₃ epilayer, where the Pt electrode is intact. The tilted sidewall around the Pt electrode can be explained by the depletion region formed between the Pt contact and α -Ga₂O₃. The dependence of the roughness on time and etching depth for each temperature condition is shown in Fig. 4(d). The surface roughness increases exponentially with the increase in temperature, which is a similar trend to that observed for the etching rate. RMS roughness exhibits a rapid increase during etching at high temperatures. To achieve

$$R = \frac{I_{\text{light}} - I_{\text{dark}}}{PS}. \quad (3)$$

$$D^* = \frac{RS^{0.5}}{(2eI_{\text{dark}})^{0.5}}, \quad (4)$$

where S is the effective area and e is the charge of an electron. The photo-to-dark current ratio (PDCR), which represents the sensitivity of the PD, was estimated to be $4.73 \times 10^5\%$ using the

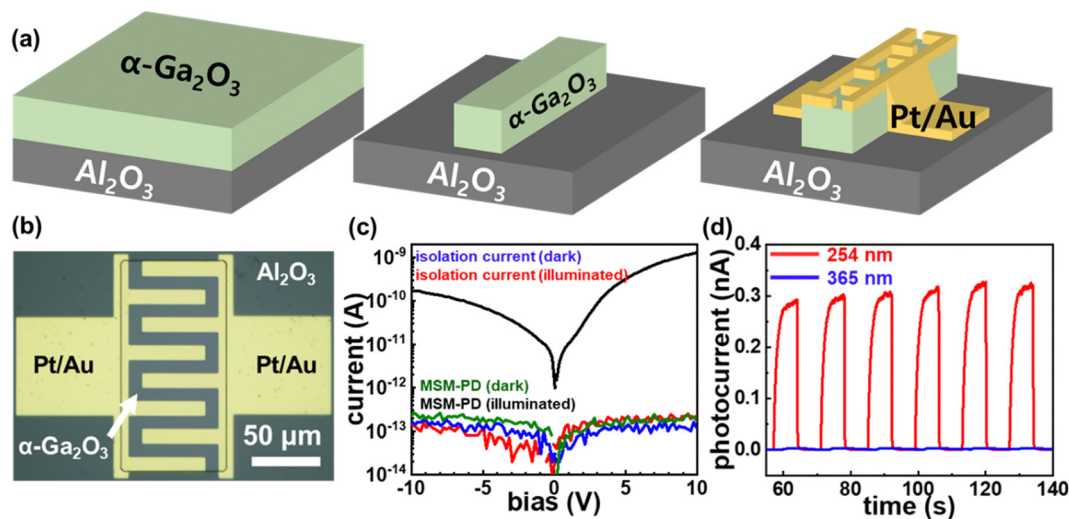


Fig. 5 (a) Schematic of the metal-semiconductor-metal photodetector (MSM PD) fabrication process. (b) The optical-microscope image of the produced PD. (c) I - V characteristics of the PD and isolated current under 254 nm UV irradiation/dark condition. (d) Time-dependent photoresponse characteristics of the fabricated MSM PD under 254 and 365 nm UV irradiations.

Table 1 Photoresponse parameters of the MSM PD under 254 nm UV irradiation (power density: 2.8 W m^{-2} ; bias: 5 V)

Wavelength (nm)	R (A W^{-1})	D^* (Jones)	PDCR (%)	Rise time (s)	Decay time (s)
254 (UV-C)	0.017	2.6×10^9	3.53×10^4	0.34/1.2	0.07/0.07
365 (UV-A)	7.0×10^{-5}	1.0×10^7	2.7×10^2	0.16/3.3	0.12/1.6

following equation:

$$\text{PDCR} = \frac{I_{\text{photo}}}{I_{\text{dark}}} \times 100\%, \quad (5)$$

where, I_{photo} is expressed as $I_{\text{light}} - I_{\text{dark}}$. The photoresponse characteristics of the fabricated MSM PD are summarized in Table 1, which indicates the high performance of our MSM PD fabricated by the PE-MAC etching. The time-dependent photoresponse characteristics were obtained *via* repetitive on/off cycles under these conditions (Fig. 5(d)). They exhibited stable and reproducible photoresponse characteristics without persistent photocurrent (PPC), which is generally observed in an oxide-based photodevice owing to the defective sites such as oxygen vacancies. J. Bae *et al.* reported the PPC effects in an α - Ga_2O_3 -based MSM PD because the mid-gap state in α - Ga_2O_3 makes it active to UVB/A regions.³¹ In our experiments, the rejection ratio (2.4×10^2), calculated as $R_{254\text{nm}}/R_{365\text{nm}}$, indicates that few mid-gap states existed in α - Ga_2O_3 after PE-MAC etching. The on/off cycles shown in Fig. 5(d) are plotted as a bi-exponential function to obtain the rise and decay time constants (Fig. 6). The bi-exponential function is given by

$$I(t) = I_0 + Ae^{-t/\tau_1} + Be^{-t/\tau_2}. \quad (6)$$

Here, I_0 is the dark current, A and B are constants, and τ_1 and τ_2 are time constants.³² The time constants in the rise domain were $\tau_{r1} = 0.70 \text{ s}$ and $\tau_{r2} = 1.97 \text{ s}$, and those in the decay domain were $\tau_{d1} = 0.03 \text{ s}$ and $\tau_{d2} = 0.83 \text{ s}$. The rise/decay time constants of the UV-C MSM PD fabricated using PE-MAC etching were compared with the results reported in β - Ga_2O_3 -based PD

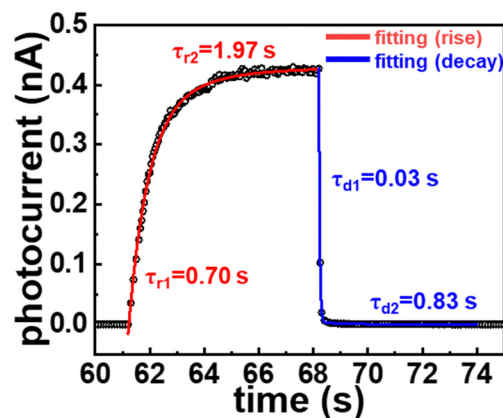


Fig. 6 Bi-exponential curve fitting of photoresponse to irradiation with 254 nm UV light.

fabricated using conventional SF_6 -based plasma etching methods, which employed a capacitively induced plasma etcher operating at 150 W and 13.56 MHz.³³ The PE-MAC-etched PD recorded notably lower τ_1 and τ_2 , linked to intrinsic band-to-band transitions and slow reactions related to surface oxygen species or defects, respectively.^{5,34} The decrease was significant in τ_2 than τ_1 in both rise and decay. Significantly lower τ_2 implies a significant reduction in plasma-induced damage with PE-MAC etching compared with conventional plasma etching. We also confirmed the electrical isolation by comparing the current of the active region and the current at adjacent electrodes. For further analysis of the defects in the fabricated UV PD,

we investigated the spectral selectivity, which is shown in Fig. 5(c); this figure also demonstrates that the electrical isolation by the PE-MAC etching is extremely effective because the isolation currents between the active layer are nominal even under UV-C illumination. Our PE-MAC etching maintained the solar-blind characteristics of α -Ga₂O₃ without creating a mid-gap state while achieving electrical isolation. The PE-MAC etching, which enables rapid etching at room temperature while maintaining crystallinity, is a highly promising technique for the fabrication of optoelectronic/electronic devices to exploit the potential of α -Ga₂O₃.

Conclusion

We identified the mechanism of PE-MAC etching by applying it to a HVPE-grown α -Ga₂O₃ epilayer, and achieved stable, damage-free, and highly anisotropic wet etching. We also evaluated the performance of this technique by fabricating electrically isolated MSM PD devices by PE-MAC etching and demonstrated anisotropic etching by irradiating the sample with a short-wavelength light source to generate EHPs, using patterned Pt metal catalysts to withdraw electrons. The patterned Pt metal remained intact and could be removed when necessary. PE-MAC etching yielded an etching rate of 8.24 nm min⁻¹ at room temperature with a smooth sidewall, and the reaction progress increased linearly with time. An activation energy of 0.90 eV (86.7 kJ mol⁻¹) was obtained from the Arrhenius plot of the etching rates at various temperatures. The linearity of the extent of reaction over time, high activation energy, and rapid increase in the etching rate with increase in temperature indicate that the PE-MAC etching of α -Ga₂O₃ is an activation-controlled reaction. The reaction mechanism is governed by an activation-controlled reaction, and the observed etching rate of several nanometers per minute at room temperature makes PE-MAC etching a promising method for electronic device fabrication. Time-dependent photoresponse characteristics from the MSM PD devices electrically isolated by PE-MAC etching were considerably improved; this confirmed that PE-MAC etching is a damage-free removal process that maintains crystal quality. The simplicity and vacuum-plasma-free characteristics of PE-MAC etching, as well as its high etching rate at room temperature and ability to prevent the formation of defects, indicate that it is a viable method for manufacturing electronic and optical devices based on α -Ga₂O₃.

Author contributions

Woong Choi – experiments, data analysis and writing. Dae-Woo Jeon – sample preparation, review and editing. Ji-Hyeon Park – sample preparation, review and editing. Dongryul Lee – data curation, methodology, review and editing. Soobeen Lee – investigation, data curation and review. Kwang Hyeon Baik – review and editing. Jihyun Kim – supervision, conceptualization, writing, review and editing.

Conflicts of interest

There is no conflict to declare.

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