Effects of the Photoelectrochemical Etching in Hydrogen Fluoride (HF) on the Optoelectrical Properties of Ga$_2$O$_3$

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Abstract. Photoelectrochemical (PEC) etching is preferred to produce micro- and nano-structures for constructing Ga$_2$O$_3$-based electronics and optoelectronics, owing to its numerous controllable parameters. During the devices fabrications, beyond the wet chemical and dry (plasma) etching produces, PEC etching also leads to device degradations inordinately. In this work, the Ga$_2$O$_3$ thin film was PEC etched by hydrogen fluoride (HF) etchant, and its optoelectric deep-ultraviolet sensing performances, including photo-to-dark current ratio, responsivity, and response speed, before and after PEC etching were analyzed and discussed.

1. Introduction

Traditional narrow bandgap semiconductors, such as Si and GaAs, deep-UV photodetectors are not real solar blindness, as a result that additional visible light blocking filters are indispensable. As far as it goes, their relevant commercial solar-blind detectors are bulky, fragile and high voltage driven [1, 2]. Wide and ultra-wide bandgap semiconductors, to some degree, could evade such a trouble in constructing photodetectors owing to their well-suited natural energy-band gaps [3-5]. Gallium trioxide (Ga$_2$O$_3$), as one of the ultra-wide bandgap semiconductors, is making an inroad in true solar-blind ultraviolet (UV) photo-detecting devices [6, 7], benefiting by its bandgap of ~4.9 eV [8, 9], allowing its high solar-blind UV/visible light rejection ratio. The same as any semiconductor devices constructions [10, 11], the etching procedures are required to perform patterning transfer in Ga$_2$O$_3$-based electronics and optoelectronics [12].

In spite of that Ga$_2$O$_3$ is up against the etching difficulty due to its high chemical robustness and bonding strength. Wet chemical etching of Ga$_2$O$_3$ has been carried out in HCl [13], H$_2$SO$_4$ [13, 14], KOH [13, 15], HF [13, 16], H$_3$PO$_4$ [14, 17], NaOH [13] and HNO$_3$ [13] solutions of a certain concentration. Of which, the etching rate and roughness are not very satisfied. In addition to that, plasma (dry) etching always cause the serious damage of the surface of the Ga$_2$O$_3$ that affect the carrier transports in relevant devices on account of the defect-related mechanisms [18-20]; such as etchants of BCl$_3$/Cl$_2$/Ar [21,22], Cl$_2$/Ar [22-24], SF$_6$/Ar [18,22], SF$_6$/BCl$_3$ [25], BCl$_3$/Ar [22,24,26], CHF$_3$/Ar [22], O$_2$/Ar [22] inductively coupled discharged plasmas. Recently, photoelectrochemical (PEC) etching technique is performed to etch Ga$_2$O$_3$, of which the external voltages and light irradiations are assistant to finish the Ga$_2$O$_3$ etching processes. B. Alhalaili et al. [27] studied the effects of the electrolyte concentration, anodic voltage, and etching time on the etching results in KOH etchant. Moreover, Y.H. Chio et al. [28] used H$_3$PO$_4$ etchant to perform the PEC etching of Ga$_2$O$_3$ and
further investigated its opto-electrical performances assisted by UV light source, showing decent photo responses.

UV photodetectors are placed huge hopes for applications in deep space detection and aviation communications; in which photodetectors may well encounter harsh detecting environments. For instance, strong acid exists extensively in the universe, which may corrode the photodetectors when it is detecting UV-ray and X-ray in the space station, leading to a degradation of device performances. Or to say, the developed wearable UV photodetectors are also in demands for its corrosion-resistant characterizations. Therefore, to investigate the corrosion-resistant property of detecting devices are urgently desired [29-31]. In this work, we perform PEC etching of Ga$_2$O$_3$ in HF etchant, and its deep-UV opto-electrical performances are analyzed. The electrical and optoelectrical characterizations before and after PEC etching are compared and discussed.

2. Experimental
The Ga$_2$O$_3$ thin film was deposited by using metal-organic chemical vapor deposition (MOCVD) method. When deposition, the triethylgallium (TEGa) and O$_2$ gas (99.999% pure) were used as Ga and O sources for Ga$_2$O$_3$ growth at temperature of 735℃ and chamber pressure of 25 Torr [32, 33]. Following which, the three-pair interdigital Ti/Au electrodes were patterned on the surface of the Ga$_2$O$_3$ films through direct-current radio-frequency magnetron sputtering. The electrodes are 3.9 mm long, 0.2 mm wide and 0.2 mm spacing distance, leading to an effective illuminated area of 0.043 cm$^2$ [34, 35]. The Ga$_2$O$_3$ films were PEC etched under irradiation of 300 W xenon lamp in 4.6 M HF etchant, the light intensity is 1000 mW cm$^{-2}$ and the anodic voltage is 10 V. After PEC etching, the Ga$_2$O$_3$ films were cleaned with deionized water and dried by N$_2$ flow gun [36]. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscope (SEM) were used to verify and discuss the quality of the film. In addition, the current-voltage (I-V) and time-dependent currents (I-t) were measured by employing the Keithley 4200 semiconductor analyzer in air at room temperature.

3. Results and Discussion
As shown in figure 1 (a) and (b), the surface of the Ga$_2$O$_3$ thin film become more flat, due to the photoelectrochemical etching effect. Through X-ray (XRD) measurement as shown in Figure 1(c), it displayed (-201), (-402) and (-603) orientations for both as-deposited and HF-corroded the Ga$_2$O$_3$ thin film, along with sharp peaks. Figure 1 (d) is the X-ray photoelectron spectroscopy (XPS) of both as-deposited and HF-corroded the Ga$_2$O$_3$ thin film. In addition, as given in figure 1 (e) and (f), the binding energy of Ga3d shift from 19.94 eV to 20.21 eV after that the Ga$_2$O$_3$ thin film is corroded by HF; and that the binding energy of O1s change from 530.57 eV to 530.96 eV.
Figure 1. The scanning electron microscope of the (a) as-deposited and (b) HF-corroded the Ga$_2$O$_3$ thin film. (c) X-ray diffraction and (d) X-ray photoelectron spectroscopy of as-deposited and HF-corroded the Ga$_2$O$_3$ thin film. The binding energies of (e) Ga3d and (f) O1s of as-deposited and HF-corroded the Ga$_2$O$_3$ thin film.

As shown in figure 2 (a), it is the linear scale current-voltage (I-V) curves of the as-deposited and HF-corroded the Ga$_2$O$_3$ thin film with Ti/Au metal electrodes in the dark. Clearly, the I-V behavior is almost Ohmic contact after HF corrosion, while it is Schottky electrical performance, due to the low carrier concentration and high resistance of Ga$_2$O$_3$ [33]. Correspondingly, Figure 2 (b) is the semi-log scale I-V curves in the dark and under illuminations, from which we can see that the photo-to-dark current ratio (PDCR) of the as-deposited beta-Ga$_2$O$_3$ solar-blind photodetector is $8.12 \times 10^5$, while it is $4.77 \times 10^2$ after HF corrosion. The high resolution HF has made a destroy for the Ga$_2$O$_3$ materials, leading to a decreased photo response.
Figure 2. The (a) linear scale I-V in the dark and (b) semi-log scale I-V in the dark and under illuminations for the as-deposited and HF-corrosion beta-Ga$_2$O$_3$ photodetector.

Figure 3. The time-dependent current of the (a) HF-corroded and (b) as-deposited beta-Ga$_2$O$_3$ photodetector.

Figure 3 (a) and (b) are the time-dependent current (I-t) performances of the HF-corroded and as-deposited beta-Ga$_2$O$_3$ photodetector, respectively. Under such two conditions, the photodetectors show decent, stable, and repeatable light switching behaviors. Under the light illuminations with intensity of 408 $\mu$W cm$^{-2}$, through fitting with $I = I_0 + Ae^{-t/\tau_r}$ where $I_0$ is stable photo current, and A is a constant, the rise time ($\tau_r$) are 1.32 s and 19.61 s for the as-deposited and HF-corroded beta-Ga$_2$O$_3$ solar-blind UV photodetectors, respectively. The decay time ($\tau_d$) are 0.84 s and 2.31 s, correspondingly.

4. Conclusion
In this work, we demonstrated the effects of Effects of the HF corrosion on the optoelectrical properties of Ga$_2$O$_3$ by photoelectrochemical (PEC) etching. The photo response and response speed for the as-deposited and HF corroded beta-Ga$_2$O$_3$ solar-blind photodetectors are all discussed in the paper.

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