Investigation of chlorine-based etchants in wet and dry etching technology for an InP planar Gunn diode*

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Mesa etching technology is considerably important in the Gunn diode fabrication process. In this paper we fabricate InP Gunn diodes with two different kinds of chlorine-based etchants for the mesa etching for comparative study. We use two chlorine-based etchants, one is HCl-based solution (HCl/H_3PO_4), and the other is Cl_2-based gas mixture by utilizing inductively coupled plasma system (ICP). The results show that the wet etching (HCl-based) offers low cost and approximately vertical sidewall, whilst ICP system (Cl_2-based) offers an excellent and uniform vertical sidewall, and the over-etching is tiny on the top and the bottom of mesa. And the fabricated mesas of Gunn diodes have average etching rates of ~ 0.6 μm/min and ~ 1.2 μm/min, respectively. The measured data show that the current of Gunn diode by wet etching is lower than that by ICP, and the former has a higher threshold voltage. It provides a low-cost and reliable method which is potentially applied to the fabrication of chip terahertz sources.

Keywords: InP etching, InP Gunn device, ICP, wet chemical etching

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1. Introduction

Gunn diodes have been commonly used for important sub-millimeter wave signal generators converting direct current (DC) into radio frequency (RF) output power.[1–4] Gunn oscillators meet requirements such as small dimension and low phase noise devices, which are essential for communication and biological or chemical sensors.[5–9] Mesa etching is often the first and most important step in developing new fabrication process. Sidewalls and profiles of mesas greatly affect the performances of the Gunn devices, such as the current and threshold voltage, and so on. Moreover, for the mesa etching, two options are available: dry etching (inductively coupled plasma or reactive ion etching) and wet chemical etching.[10–12] The two techniques have their own advantages and disadvantages. Dry etching allows an exact definition of the mesa, prevents unwanted under-etch, and provides excellent vertical side-walls, but it needs high power and high cost equipments. The wet etching (HCl-based solution) does not need expensive equipment, but the top of sidewall can hardly avoid etching, as the anisotropic characteristic of chlorine-based solution. In addition, the solution with a different mixture ratio may generate virulent gas in the etch process.

There are some drawbacks in the recent study. A dry etch (RIE) method for the InP Gunn mesa process first was reported by Proust *et al.*[10] in 1992. In their paper they used dry reactive ion etching (RIE), but some problems appeared with the method, such as carbonated polymers on the surface, slow rate ($<$ 400 Å/min), *et al.* The bottom of mesa has a rough surface from the image presented by Liu *et al.*[11] in 1998. Wet etch (HCl-based solution) method for InP Gunn mesa process was reported by Lee *et al.*[12] in 2008. They reported that tops of the mesas are circles, while the bottoms of the mesas are rectangles. However, in the present work, we fabricate the InP Gunn diodes from two different chlorine-based etchants for mesa etching. The side-walls of mesas by wet etching and dry etching show excellent vertical uniformity, and are better than those obtained by Liu *et al.*[11] and Lee *et al.*[12] We also achieve very good negative differential resistance (NDR) curve.

2. Fabrication of InP Gunn diodes

The epitaxial structure[10,13,14] was grown on a 2-inch, 370-μm thick, and semi-insulating (SI) InP substrate by molecular beam epitaxy (MBE). The layers were a 300-nm InGaAs n+ layer doped over level of 2×10^{18} cm^{-3}, a 1.8-μm-thick n+ InP buffer layer doped at a level of 1×10^{18} cm^{-3}, a 1.5-μm-thick InP active layer doped with Si at 1.1×10^{16} cm^{-3}, and a 0.3-μm-thick n+ InP contact layer

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doped with Si at 2×10^{18} cm^{-3} as shown in Fig. 1.

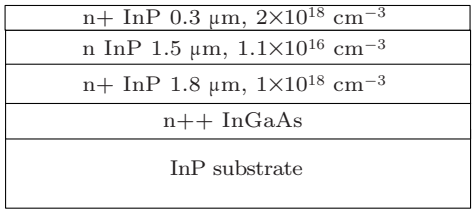


Fig. 1. Epitaxial structure of the InP Gunn diode.

Figure 2 shows the Gunn diode fabricated by the following steps. Firstly, the circle metal pattern of cathode was formed by photolithography technique using AZ 5214 photoresist (PR). The contacts were then formed by evaporating Au/Ge/Ni/Au (900/500/300/2000 Å) on the low doping layer (active layer) using electron beam evaporator. The PR was then stripped off. Secondly, the cathode was protected by a mask layer. In this work, the mask varied with the etching methods. In wet chemical etching, the mask layer was formed by using the photolithography technique using 9920 PR. While in dry etching (ICP), the mask layer was formed by an SiO_2 layer deposited by plasma enhanced chemical vapor deposition (PECVD). In the present experiment, the mask layer was prepared using evaporator Ti metal layer (3000 Å) instead of SiO_2 layer. Thirdly, mesas etching were performed by wet chemical etching and dry etching, respectively. Then the mask layer was stripped off. PR would be dissolved in an acetone, while the SiO_2 and Ti mask layer were easily removed in a hydrofluoric acid (HF) dilution solution. HF and acetone were not aggressive for InP substrate. Futhermore, the Ti metal layer was etched clearly in the ICP etching process. In order to gain a comparative study, we used two different chlorine-based etchants: one was a wet chemical etching in a solution of HCl-based etchant ($\sim$37.5% HCl : $\sim$ 85.5% H_3PO_4 = 1 : 4), and the other was Cl_2/Ar gas mixture in ICP system. The etching rates were approximately 0.6 μm/min and 1.2 μm/min, respectively.

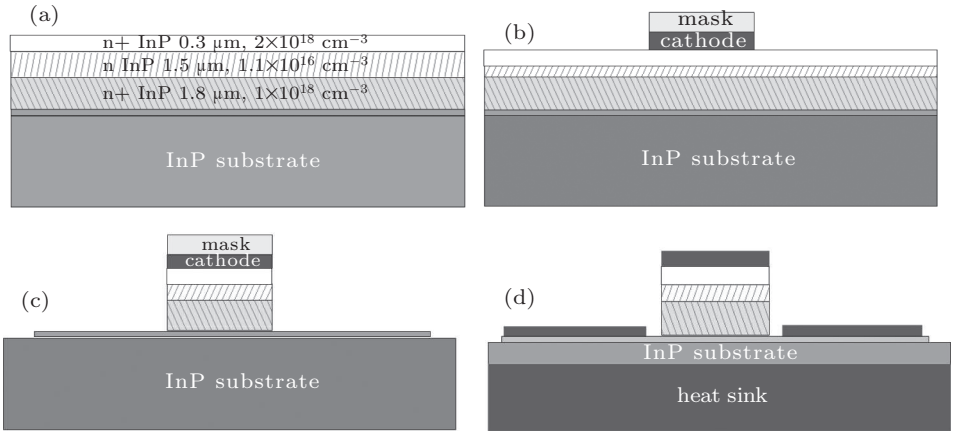


Fig. 2. Fabrication procedure of the InP Gunn diodes. (a) MBE and wafer cleaning, (b) mask layer and metallization of cathode, (c) mesa, and (d) metallization of anode and heat-sink (HS).

Fourthly, the circle metal pattern of cathode was formed by using 4400 PR to open the windows on the exposed InGaAs layer, followed by evaporating the same metal layers as cathode metal layers. Then the samples were annealed at 590 K for 60 s. Finally, the InP substrate was thinned by lapping and polishing, and then a heat sink seed layer was formed using RF magnetron sputtering. A 25-μm-Au heat sink was electroplated. The Au plating was performed with a DC current density of about 100 mA/cm^2 and a plating solution temperature of 60 °C for 25 min. If the diodes were mounted on diamonds, the power efficiency would increase.[14,15]

3. Wet and dry etching mesa of InP Gunn diode

Figure 3 shows the results of chlorine-based wet chemical etching. In the etching process, it was observed that it would bring out gas between InP layers and the etching solution. The gas still stayed on the InP layer in the form of bubbles. The bubbles would keep the wet chemical etching solution off the InP layers. In order to achieve a smooth and uniform surface, the mesa was etched in the HCl-based solution under an ultrasonic condition and a fixed temperature. In this way, the number of bubbles was decreased and the etching rate could keep nearly uniform. We found that the sidewalls were nearly vertical, and the bottoms of mesas were approximately circles. The rectangular shape bottoms of the mesa of InP Gunn diodes failed to appear in this chlorine-based etchant. Hence, it was better than chlorine-based etchant of the wet chemical etching mesa by Lee *et al.*[12] (Fig. 3). As a result of the anisotropic characteristics of the etchant, the profile views (a) displays excellent vertical side wall and a tiny slope on (010). So it is proved that the etching rate of vertical direction is much faster

than that of the lateral direction but the etching on (010) was a little slower than those in other directions in this solution. We found that if the etching time was properly delayed, the slope would disappear in this chlorine-based etching solution as shown in Fig. 3(b). Moreover, as the self-stop etching layer InGaAs layer can stop effectively this solution etching in vertical direction, but cannot stop lateral etching. Therefore, the etching time of mesa needs to be controlled accurately and it is better to repetitiously etch the mesa and observe the mesa height and side-wall profile to gain excellent etching performance

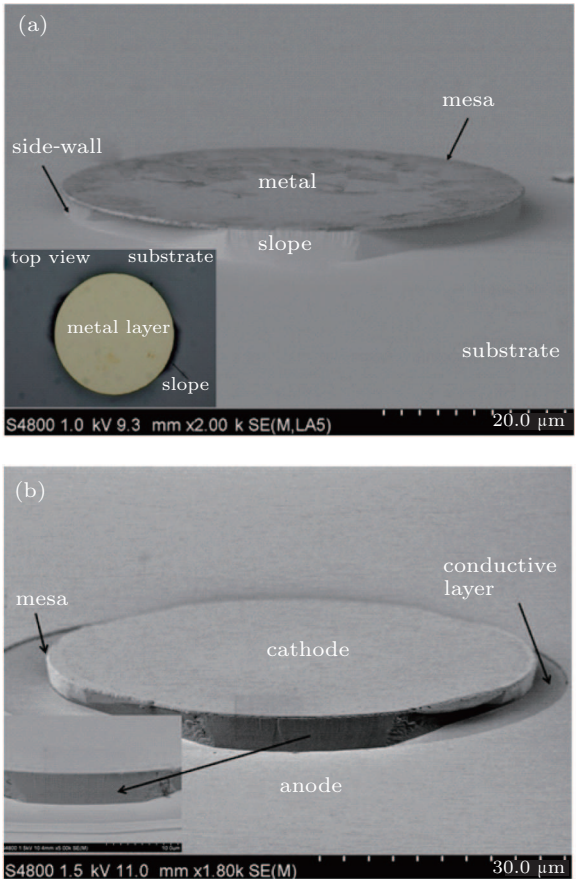


Fig. 3. (color online) Scanning electron microscope (SEM) images of fabricated etching InP mesas. (a) Top side view and profile view of wet etching InP substrate, showing a normal circular cathode and an excellent vertical side wall. (b) Gunn diode etched in wet chlorine-based solution for proper time, showing an excellent vertical side wall without the slope.

The dry chlorine-based etch was performed in inductively coupled plasma system (ICP SENTECH SI 500). The conditions were as follows: the gas mixture composed of Cl_2 (12 sccm), Ar (3 sccm) ; the total pressure at 0.5 Pa, the beginning gas press at 0.3 Pa; the RF power at 100 W, and the source power at 300 W. The bias voltage was around -145 V. In this work, the temperature was kept at (100 ± 1) °C, resulting in an etching average rate of 1.2 μm/min. The etch-rate was monitored by sampling the etched thickness with a plasma monitor and a Dektak Profilometer (Dektak 200).

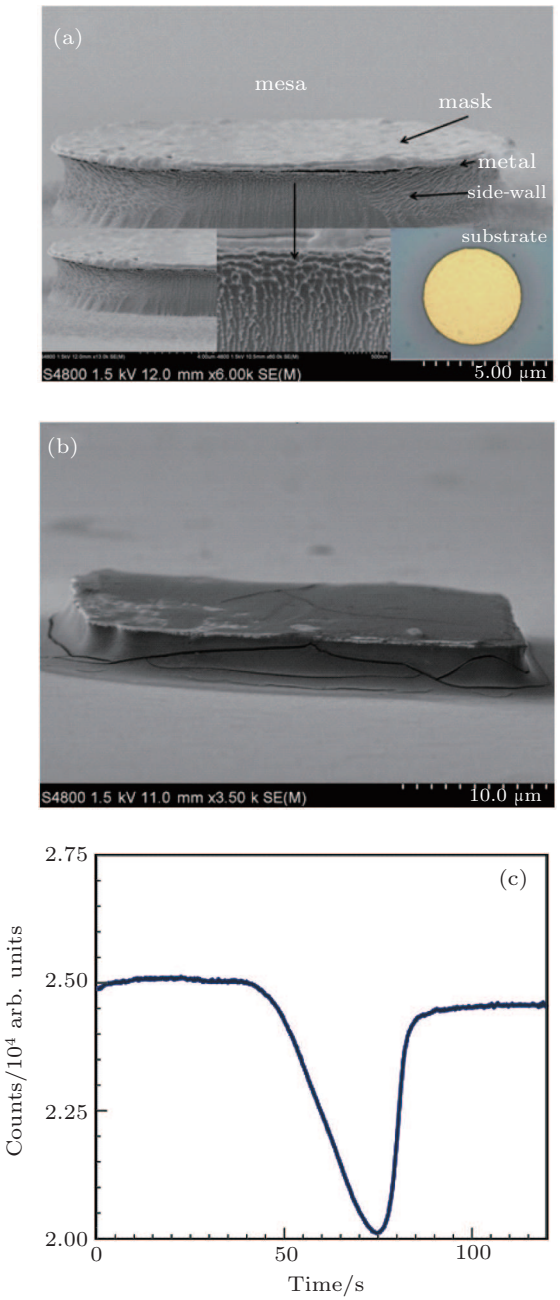


Fig. 4. Etching mesa formed by ICP. (a) The profile of InP mesa formed by ICP, showing a little over etching and regular frills on the side-wall and a top view of a normal circle. (b) The cracks on the mesa, indicating the transverse cracks on the side-wall and irregular cracks on the top surface. (c) The monitor etching data by plasma monitor.

Figure 4 shows the mesa, which is etched by Cl_2/Ar gas mixture (ICP). The gas of Cl_2 is the etchant, and the gas of Ar is buffer gas. Different conditions lead to evidently different performances. The top view of mesa exhibits a good circle and the various side-walls are approximatively the same in Fig. 4(a). Some regular frills are formed on the side wall and the bottom of the mesa in dry Cl_2/Ar etching process. The number of frills is distinctly reduced by raising the gas press, but it would induce InP mesa cracks (b). Therefore, the total

gas press should be carefully optimized to prevent the frills and cracks from appearing. In our work, it was 0.3 Pa $\sim$ 0.5 Pa. Moreover, the rate is varied in etching process under the unchanged etch condition. Figure 4(c) shows that the etching rate is very low in the first 40 s by Dektak Profilometer, and it becomes gradually high after 40 s. By the way, the different masks of nickel or titanium metal layer have been used in our recently work, respectively. The mask of nickel metal layer is better than SiO_2, and the mask of titanium layer is best in all layers.

Through various experiments, the condition of ICP was optimized to make sure that about 2-μm height mesa and the 10 μm$\sim$ 40 μm pattern of cathode are needed for proper etching time and method in order to monitor and control it. The powers (RF power and source power) were reduced, resulting in a low etching rate, not only the InP layer could be etched every slowly but also Ti metal was etched off. Then the Au metal layer (under the Ti mask layer) was also etched off. On the other hand, if the powers were too high, the rate of etch was faster, possibly resulting in the over etching or bringing on a bad effect of the contact electrode. The heights of the mesas under various etching times in the ICP system, are shown in Table 1.

Table 1. Heights of mesas with different sizes (10 μm–40 μm) of the mesa prepared in ICP under the above etching condition (the metal layer of cathode and the mask layer are both about 770 nm).

Time/s	Height/nm
3 0	810∼840
5 0	1092∼1230
6 0	1302∼1520
7 0	1653∼1734
8 0	1905∼1947
9 0	2133∼2296

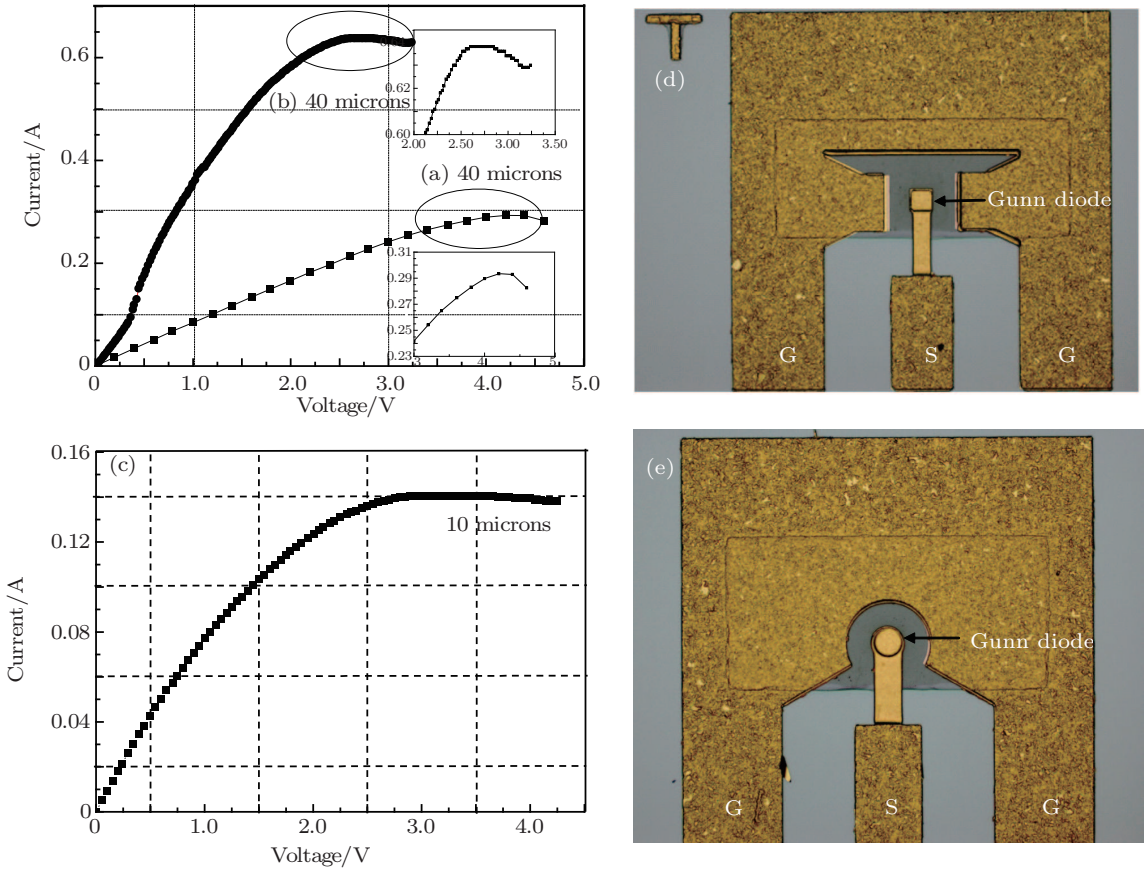


Fig. 5. (color online) Plots of the current–voltage for Gunn devices with different etching mesas and the same layer structures. (a) The mesa (40-μm hight) etched by HCl/H_3PO_4 solution. (b) The mesa (40-μm hight) etched by ICP in Cl_2/Ar gas (40 micrions). (c) The mesa (10-μm hight) etched by ICP in Cl_2/Ar gas. (d) Gunn diode with a rectangle electrode. (e) Gunn diode with a circle electrode.

The advantages of the InP Gunn diode lie principally in the higher drift velocities of electrons, due to the more pronounced NDR. Forward voltage is applied to the anode (on the bottom of device). The electrons injected from the cathode flows to the anode through the transit region (from the Γ-valley to the L-valley).[16] Figure 5 shows the current–voltage characteristics of several fabricated Gunn diodes, measured by Cascade 12 K system. The cathode sizes of Gunn diodes are both 40 microns. The currents are 295 mA and 645 mA, and the threshold voltages are 4.0 V and 2.7 V, respectively. As

the mesas of the Gunn diodes are formed by different methods, especially the wet chemical chlorine-based etching may be aggressive for metal layers of the electrodes of Gunn diode. The current of the Gunn diode formed by wet etching was smaller than that of the same-sized Gunn diode formed by ICP. The small-sized Gunn diode has smaller current in the same etching condition. Figures 5(a) and 5(c) show that the Gunn devices with different diameters have different peak currents. The threshold voltage of Gunn diode formed by wet etching is larger than that by ICP. Moreover, the current of the Gunn diode formed by wet etching in HCl-based solution is larger than that by wet etching, given by Choudhury *et al.*[17] and Lee *et al.*,[12] whilst the current of Gunn diode formed by ICP etching is larger than that by dry etching, given by Liu *et al.*[11] Figures 5(d) and 5(e) show the planar Gunn devices with test pad structures. By the way, ICP etching has better performances for the whole process flow.

4. Conclusions

In summary, InP Gunn diodes are designed and fabricated for millimeter wave devices by using two kinds of chlorine-based etching methods. Results prove that chlorine-based etchants in wet and dry etching technology can gain excellent mesa profiles for InP planar Gunn diodes. In the wet chemical chlorine-based solution, the mesa could be easily controlled and brought out. The side-walls are approximately vertical. The surfaces on the side-wall are smoother than those formed by dry etching, which are also found in the papers by Lee *et al.*,[12] Proust *et al.*,[10] and Liu *et al.*[11] While in the dry Cl_2/Ar etching (ICP), the trend of mesa variation is almost uniform in perpendicular direction. Moreover, the currents of the same epitaxial structure and the same-sized Gunn diodes are 293 mA and 645 mA, and the threshold voltages are 4.0 V and 2.7 V, referring to chlorine-based wet etch and dry etch. In addition, in the same etching condition, the smaller size Gunn diode has smaller current.

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