

Plasma Etch Induced Surface Damage and its Impacts on GaAs Schottky Diodes

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INTRODUCTION

Dry etch plays a very important role in fabrication of modern III-V compound semiconductor devices. Compared to wet chemical etch, dry etch, which uses reactive gas plasma to remove substances chemically, has many advantages, such as better controllability, higher pattern reproducibility, and lower cost. Dry etch can induce surface damages that will affect physical and electrical properties of devices, due to high energy ion bombardments and the presence of reactive ion species [1-10]. These damages include surface roughness due to ion bombardment, surface contamination due to polymer deposition, and surface stoichiometry change due to preferential etching or layer intermixing. Highly damaged surfaces are least favored since the surfaces are not reproducible and cause high degree of non-uniformities in the electrical performances of the devices.

This paper will show that by comparing the barrier height measured from a large area Schottky diode, the GaAs surface damage can be characterized in terms of different dry etch parameters so that dry etch processes can be optimized to produce the desired patterns on GaAs, while minimize the GaAs surface damage to a certain extent.

EXPERIMENTAL

A parallel plate capacitively-coupled plasma etcher is used, in which the reactive gases come out of a shower head and are converted into plasma by applied RF power at 13.56 MHz on the top electrode. A GaAs wafer, with nitride protection, sits on the bottom electrode plate that is connected to ground. Bias is measured on the top electrode on this tool. The reactive gases are a mixture of $CF_4/CHF_3/O_2$. A Schottky contact with total area of $400 \mu m^2$ is defined by patterning the wafer with photo resist and etching the protection nitride away to expose the GaAs surface. A Ti/Pt/Au Schottky contact metal is deposited on the exposed GaAs surface.

Impacts of RF power, gas flow rate, time, and electrode temperature were studied in terms of Schottky barrier heights measured by C-V method. To investigate the depth of the damaged GaAs layer, different wafers were also subjected to $NH_4OH:H_2O_2$ solution so that the damaged GaAs layer can be removed after dry etch and barrier heights were measured on these wafers to determine the depth of the damage layer.

DISCUSSION

When the Schottky contact is defined by the dry etch process, surface states caused by plasma damage will impact electrical characteristics of the Schottky diode such as its effective barrier height, turn on voltage, reverse-biased leakage current, and breakdown voltage. By the tool design, the ion bombardment is

minimal in such a system since there is no applied DC bias. Most surface damage is induced by fluorine ions chemically etching the GaAs surface, polymer dumping during etch, and surface oxidation. Figure 1 shows the impact of dry etch RF power on GaAs Schottky barrier height. An increase in RF power during etch from 250 W to 450 W resulted in a 20 mV reduction in the barrier height. Higher RF power will provide more energy for ionization and increase plasma density to cause more fluorine ions in the plasma, hence induce more chemical etching and more damage to the GaAs surface. These damages are formed by GaAs broken bonds and dislocations due to etching and ion bombardment, which become carrier traps. The effective barrier height is reduced due to hopping conduction through aligned carrier traps, from GaAs valence band to its conduction band [11-13]. Surface damage will also cause more electrons tunneling from GaAs to the Schottky contact metal. Subjection of these wafers into further processing, such as diluted hydrochloric acid (HCl) dipping, prior to Schottky contact metal deposition, will further reduce the barrier height, as also shown in Figure 1. HCl can preferentially etch gallium and leave un-bonded arsenic behind to reduce GaAs barrier height[14]. Interestingly, after HCl dipping the wafer etched at 450 W showed ~10 mV higher in barrier height, compared to the wafers etched at 250 W. At high RF power the fluorine plasma is creating much higher damage to the GaAs surface so that the barrier height decreases with increased RF power after etch. However, the higher damage density on the GaAs surface is also preventing the plasma ions penetration underneath the surface so that at higher RF power the damage depth is shallower compared to the low RF power case, even though the damage density on the GaAs surface is higher.

Figure 2 shows the impact of dry etch electrode temperature on the GaAs barrier height. When the dry etch temperature is increased, the silicon nitride etch rate is also increased. This is reflected in the critical dimension measurements. A 13 degree increase in the electrode temperature results in a 72% increase in the critical dimension, from $1 \mu m$ to $1.7 \mu m$. Higher temperatures result in higher desorption rate of reaction byproducts and lower polymer re-deposition rate onto the GaAs surface, causing a kinetics change at the surface so that the GaAs surface is more exposed after nitride etching and the resultant surface damage is more. The barrier height decreases at higher etch temperature. However, when the temperature is further increased the barrier height does not decrease any further. Instead, the barrier height increases slightly and shows a recovery. This is believed due to the reason that at higher temperature the surface damages will have higher mobility and diffuse inwardly.

Figure 3 shows the impact of CF_4/CHF_3 ratio on the Schottky barrier height. Increasing in CF_4 while decreasing CHF_3 produces fewer polymers on GaAs surface and provides less protection to the GaAs surface during etch. Higher CF_4 flow rate will result in an increase in the fluorine ion density in the plasma and more

reaction to the GaAs surface. The barrier height decreases with increased CF_4/CHF_3 ratio. However, in capacitive plasma chamber the overall fractional ionization rate is very low, usually in the 0.01% range, e.g., 1 molecule in 10000 is ionized. Changing CF_4/CHF_3 ratio from 2:1 to 4:1 does not change the plasma density significantly; nor does it change the fluorine ion concentration in the plasma significantly. That is the reason that during this set of experiments the barrier height has only lowered from 0.81 V to 0.78 V. The effects of RF power and temperature have much higher impacts than changing the CF_4/CHF_3 ratio.

Prolonged etch will also have a negative impact on the barrier height. Longer etch time means longer ion bombardments to the GaAs surface and more chemical reactions between fluorine ions and the GaAs surface. Figure 4 shows the effect of longer dry etch time on the barrier height. As expected, the GaAs Schottky barrier height decreased from 0.81 V to 0.76 V as the etch time increases from 95 seconds etch to 114 seconds. During this experiment the RF power, temperature, and CF_4/CHF_3 ratio were all kept at the low end. Etching the GaAs surface with 40% longer time will not have further impact on the barrier height. As shown in Figure 4, etched at 133 seconds the barrier height remained exactly the same as etched at 114 seconds. Surface damage incurred during the initial etch acts like a protection layer to prevent the GaAs surface from ion attacks associated with longer exposure in the plasma.

Damaged layer removal was performed by etching the wafers in 1:1 $NH_4OH:H_2O_2$, De-ionized-water solution. A series of wafers were rinsed in the above solution with different times, and etch depth was measured using a P-22 Tencor profilometer. The etch depth is shown in Figure 5. The etch rate, e.g., the slope of the polynomial line in Figure 5, is almost same at the first 20-30 seconds and then starts to level off, indicating that the damaged GaAs was etched faster than un-damaged GaAs.

Figure 6 shows the barrier heights measured on these wafers after damage removal. Since after wet etch these wafers went through all the processing steps including the HCl dipping, the wafers etched at 250 W RF power and showed relatively the same barrier heights as those etched at 450 W RF power, as shown previously in Figure 2. The 450 W wafer without any damage removal showed a slight higher barrier height due to the reason that in higher power etch the GaAs damage is closer to the surface and the subsequent processing cycles can anneal and repair these damages more easily. In comparison, damages induced by low RF power etch can penetrate deeper in the bulk GaAs so that the damaged GaAs is less repaired after processing cycles and the barrier height shows less recovery. When the surface damage is removed by the ammonium-peroxide solution the barrier height recovered. After 600 Å damage removal the barrier height increases close to around 0.82 V, which is believed to be the theoretical value of GaAs Schottky contact [15]. This indicates that dry etch damage starts from the surface and get into the GaAs surface as deep as ~600 Å. These damages underneath the surface are either due to plasma ion penetration during the dry etch process, or, formed during subsequent processing cycles after dry etch. The top damage surface, which contains dangling bonds and vacancies, will enable underneath gallium or arsenic atoms to move upwards and try to occupy the vacancies, thus, the damages will diffuse into the GaAs and the damaged layer will grow thicker over time.

Figure 7 shows the barrier height as a function of AC frequency used in the C-V measurements. At low frequency the barrier height is higher. There is an apparent cutoff frequency and using frequencies beyond that will not affect barrier height measurements. As indicated in Figure 8, the cutoff frequency in this case is about 2000 Hz and all the barrier heights measured using frequency higher than this 2000 Hz are essentially the same. This brings up an interesting point since the theoretically calculated barrier height based on equations (1) and (2) should be independent of frequency. The measured capacitance of the Schottky diode shows the same trend, as shown in Figure 8. The capacitance is higher at low frequencies and beyond 2000 Hz the capacitance is relatively unchanged.

$$C = \frac{\epsilon_s}{w} = \sqrt{\frac{q\epsilon_s}{2(\phi_i - V_a)}} \frac{1}{N_d} \quad (1)$$

$$\frac{1}{C^2} = \frac{2}{q\epsilon_s N_d} (\phi_i - V_a) \quad (2)$$

In the above equations, C is the capacitance density in F/cm^2 , ϵ_s is permittivity or dielectric constant of GaAs, which is $1.162E-12$ F/cm, q is the electron charge, $1.6E-19$ C, w is the depletion width in cm, ϕ_i is the barrier height in V, V_a is the applied voltage also in V, N_d is the silicon doping in the GaAs. Plotting $1/C^2$ against applied voltage V_a , the barrier height ϕ_i is the intercept of the curve on the voltage-axis. Equation (2) can be derived as:

$$N_d = -\frac{2}{q\epsilon_s} \frac{1}{d(1/C^2)/dV_a} \quad (3)$$

$$w = \epsilon_s A / C_t \quad (4)$$

The doping density can be calculated. The depletion width w can be obtained from equation (4), where A is the total area of the Schottky diode in cm^2 . Noting that in equation (4) C_t is the total measured capacitance instead of C, the capacitance density.

Using the analogy of a metal-oxide-semiconductor (MOS) capacitor, the capacitance induced by surface states can be treated as a parallel capacitor to the existing capacitance induced by the doping N_d [16]. The dry-etch damages, e.g. the charge traps causing surface states, are acting like capacitors due to their abilities of trapping and de-trapping electrons. These traps are much larger in size compared to the electrons so that they cannot follow the fast charging and discharging at higher frequencies. In another word, at higher frequency the only capacitor functioning is the one induced by doping. The one induced by surface states is more like a resistor at higher frequencies. At a frequency lower than 2000 Hz, the traps follow the alternation of the applied electrical field so that the overall capacitance is higher, as well as the barrier height, as shown in Figure 7 and 8, that the barrier height is changing with frequency and higher at low frequencies.

Using the equations (3) and (4), the surface state density N_{ss} can be deduced from the difference in N_d obtained from high and low frequencies. The depletion width can be calculated as 0.26 μm . The surface states density can be calculated, as shown in Figure

9. Without any damage removal the surface states density is $8.0 \times 10^{10} \text{ cm}^{-2}$ for the 450 W wafer, compared to only $3.9 \times 10^{10} \text{ cm}^{-2}$ for the 250 W wafer. This confirms that the high RF power in dry etch causes more damage to the GaAs surface. The damage profile in the 450 W case is decreasing, indicating that the damage on the GaAs surface actually prevents further ion penetration and damage to the layer underneath.

CONCLUSION

Plasma etch will induce damages on the GaAs surface by ion-bombardments and chemical reactions. Device characteristics such as Schottky diode turn-on voltage can be affected by these surface damages. It is demonstrated that using high RF power in dry-etch will cause more defects on the surface. Using lower RF power will cause less surface damage but the damage will happen deep underneath the GaAs surface, due to the plasma ion penetration and not enough damage on the surface to prevent such penetration. High temperature in plasma etch, higher fluorine concentration in the plasma, and longer etch will also induce damage to the GaAs surface and reduce the Schottky barrier height. The surface damage can be removed by wet chemical etch. Highly damaged GaAs etches faster than less damaged GaAs. After damage removal the Schottky barrier height can be recovered. It is found these damages can reside in GaAs as deep as 600 \AA , by plasma ion penetration or heat-induced diffusion.

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GRAPHS

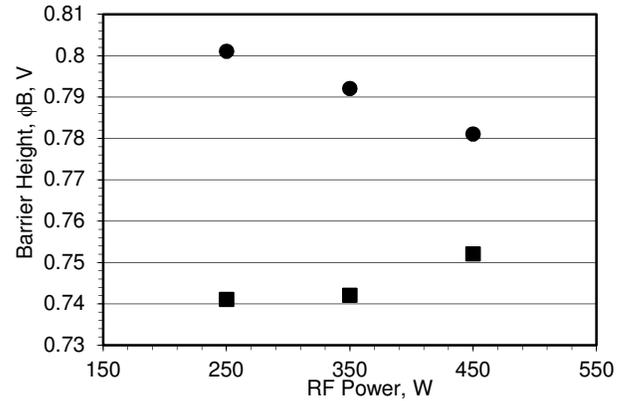


Figure 1 Impacts of RF power during etch on GaAs barrier height. (●): After contact metal deposition. (■): After HCl dipping.

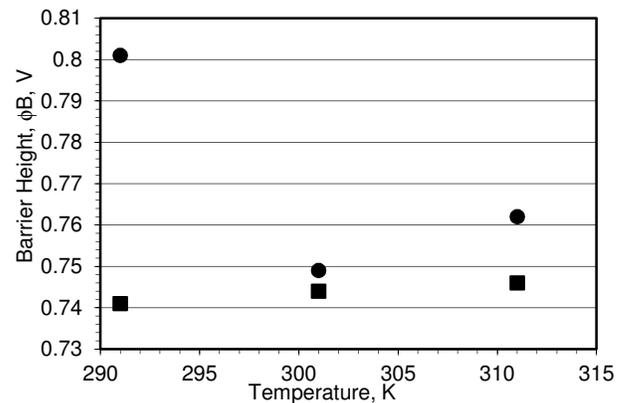


Figure 2 Impacts of electrode temperature during etch on GaAs barrier height. (●): After contact metal deposition. (■): After HCl dipping.

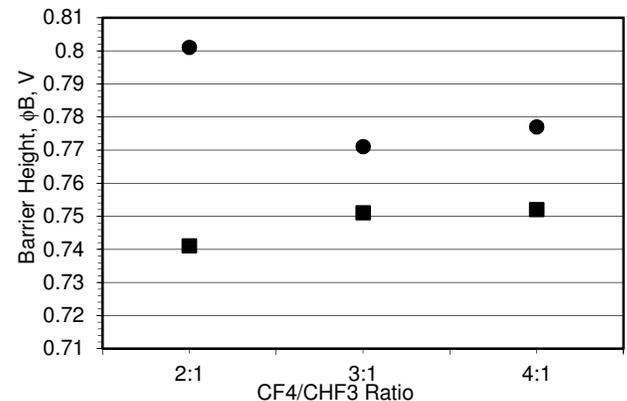


Figure 3 Impacts of reactive gas flow during etch on GaAs barrier height. (●): After Schottky contact metal deposition. (■): After HCl dipping.

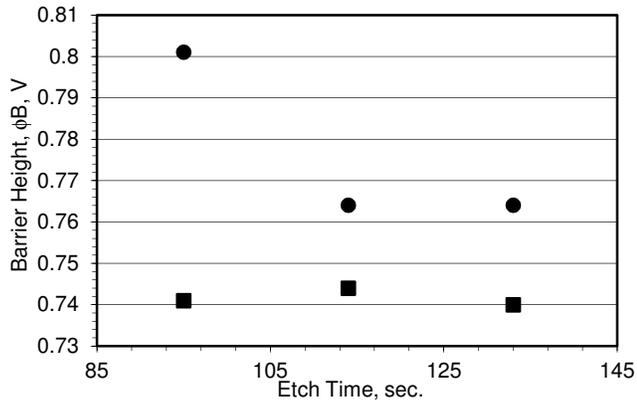


Figure 4 Impacts of time during etch on GaAs barrier height. (●): After Schottky contact metal deposition. (■): After HCl dipping.

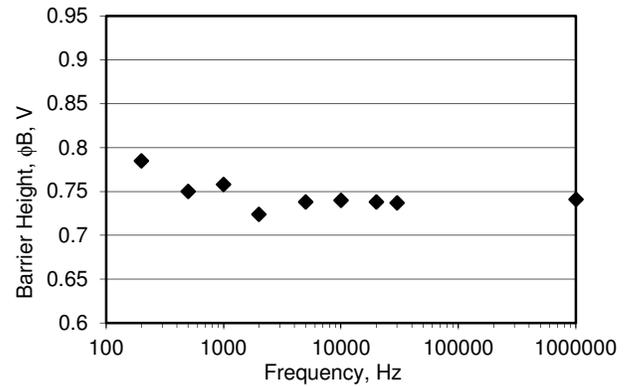


Figure 7 Barrier height measurements using different frequency. Wafer was etched with 250 W RF power.

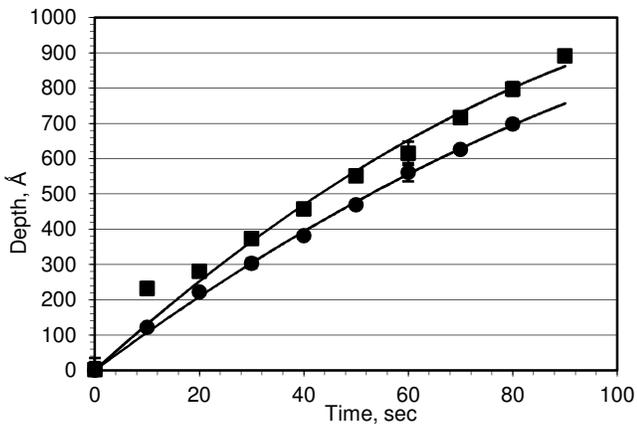


Figure 5 Damage removals in wet chemical solution after dry etch. (●): 250 W RF power. (■): 450 W RF power.

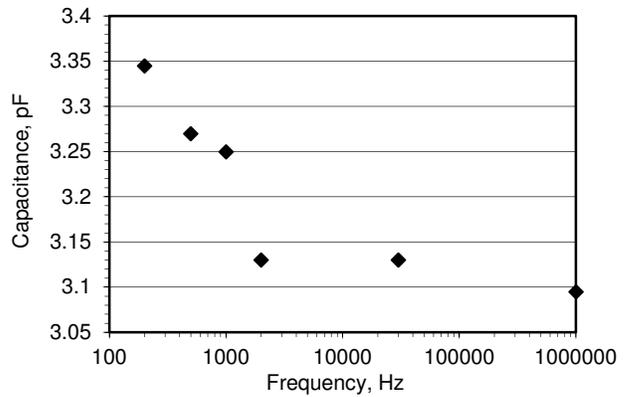


Figure 8 Capacitance at 0 V at different frequency. Wafer was etched with 250 W RF power.

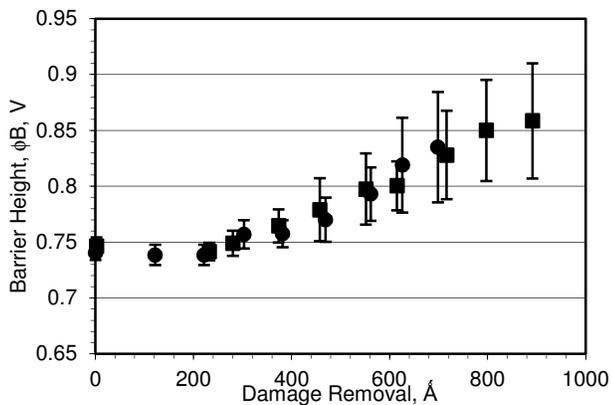


Figure 6 Barrier height measurements at 1 MHz and 25 °C after damage removal. (●): 250 W RF power. (■): 450 W RF power.

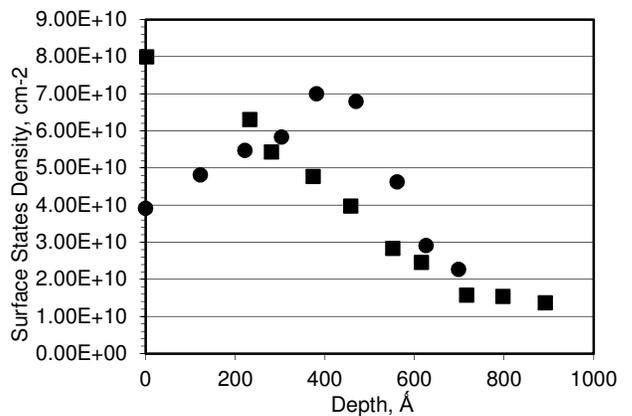


Figure 9 Surface states density calculation. (●): Wafers dry-etched with 250 W RF power. (■): Wafers dry-etched with 450 W RF power.