CF_4–Ar reactive ion etching of gallium arsenide

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A systematic study of the etch rate of GaAs and of positive photoresist for different mixtures of argon and carbon tetrafluoride was conducted over radio frequency powers (from 0.06 W/cm^2 to 0.55 W/cm^2), pressures (from 6 to 35 mTorr (1 Torr = 133.3 Pa)), and concentrations of CF_4 in Ar (0–60% with a constant mass flow of 10 sccm). Capacitance–voltage and I–V measurements on GaAs diodes made after reactive ion etching were carried out to estimate possible etching damage through thin dielectric film and surface state creation. Etch rates up to 200 Å/min were obtained on GaAs with low damage in a 40% CF_4, 20 mTorr, and 0.55 W/cm^2 plasma while the etch rate of the patterning photoresist was 600 Å/min. These results are in good agreement with those reported in literature. The ideality factors and Schottky barrier heights of reactive ion etching of GaAs are comparable to those obtained by sulphuric and peroxide acid etching. However, reactive ion etched samples seem to suffer from higher surface state densities as measured by C–V techniques.

On a procédé à une étude systématique de la vitesse de gravure sur GaAs et sur photoresist positif par différents mélanges d'argon et de tétrafluorure de carbone, en variant la puissance fréquence radio (de 0,06 W/cm^2 à 0,55 W/cm^2), la pression (de 6 à 35 mTorr (1 Torr = 133,3 Pa)) et la concentration de CF_4 dans Ar (de 0 à 60%, avec un flux de masse constant de 10 sccm). Des mesures C–V et I–V ont été effectuées sur les diodes GaAs fabriquées après gravure par CF/Ar, afin d'estimer le dommage possible par création d'un mince film diélectrique et d'un état de surface. Des vitesses de gravure allant jusqu'à 200 Å/min ont été obtenues sur GaAs, avec peu de dommage, dans un plasma de 40% CF_4, 20 mTorr et 0,55 W/cm^2, alors que la vitesse de gravure du photoresist patron était de 600 Å/min. Ces résultats sont en bon accord avec ceux qui sont rapportés dans la littérature. Les facteurs d'idéalité et les hauteurs de barrière Schottky de GaAs traité de cette façon sont comparables à ceux qu'on obtient avec l'acide sulfurique et le peroxyde. Les échantillons semblent toutefois souffrir de plus hautes densités d'états de surface, selon ce qu'on peut mesurer par les techniques C–V.

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1. Introduction

Gallium arsenide (GaAs) is an interesting semiconductor used for many applications in high speed microelectronics and optoelectronics. Many devices, like the vertical field effect transistor and waveguides with a 90° angle, require etched GaAs to produce vertical wall profiles. Among all etching techniques, the reactive ion etching (RIE) can best produce such profiles due to the high radio frequency (rf)-induced direct current (dc) electric field perpendicular to the substrate. Among the oxidizing gases generally used in the RIE of GaAs, the system CF_4–Ar was chosen for this study to provide the reactive species, for the following reasons. Unlike the usual chlorinated halogen gas mixtures, risks of corrosion and contamination to both the reactor and the pump are almost eliminated with the use of CF_4, and it is of low toxicity. Its slightly lower etch rate (1–3), compared with the chlorinated gases, is not a limiting factor in many process applications. However, a possible problem with RIE is the production of compounds on the top of the etched surface (4). The addition of argon to the halocarbon gas assures us of at least the partial sputter removal of low volatility compounds (5–7). In the case of CF_4, a thin layer of low volatility compounds such as GaF_3 forms. This paper presents a systematic study of the etch rate of {100} GaAs by CF_4–Ar RIE as a function of the various process parameters, namely, the power, the total pressure, and the CF_4 concentration.

2. Methodology

The reactor used is a Material Research Corporation (MRC) model SEM-8620 in which both RIE and sputtering are possible. During etching, the distance between the lower electrode (cathode) and the nearest grounded shutter is 6 cm. All electrodes are water cooled. The 15.2 cm (6") diameter cathode, which holds the substrates, is excited with a 13.56 MHz rf source (Plasma-Therm Inc., model HFS 500 E). Gas flows are controlled with a 2% accuracy by a mass flow controller system (Vacuum General, Model UC2-22S01, 0–10 sccm). Pressure in the reactor is controlled by throttling the diffusion pump with the high vacuum gate valve. The rf power is applied through an impedance-matching network so as to always minimize the reflected power during the entire process.

Etch depths are measured at steps in the semiconductor surface or the photoresist by a Dektak mechanical profilemeter. Steps in the GaAs were created by etching through holes in a Shipley 1400-33 positive photoresist mask applied in the manufacturer's recommended fashion and patterned photolithographically. Small cleaved pieces of silicon wafers were used to mask the photoresist to create etch steps in it. Etch rates are calculated as the ratio of the mean measured etch depth at a step divided by the total etch time. The crystals of GaAs used were liquid-encapsulated Czochralski (LEC) wafers oriented at {100} and doped-n ($N_D = 1.5 \times 10^{17}$ cm^{-3}). Samples to be etched were attached either directly to the stainless steel cathode, or to a quartz disk covering the cathode, depending on the degree of contamination observed.

3. Results and discussion

3.1. Etch rate as a function of power

Figure 1 shows the etch rate (Å/min) of the resist and the GaAs as a function of power (W) for fixed total pressure (20 mTorr) and a fixed geometry (samples lying directly on a bare stainless cathode). The uppermost line shows the etch rate of the resist in an inert atmosphere of pure Ar. The two remaining

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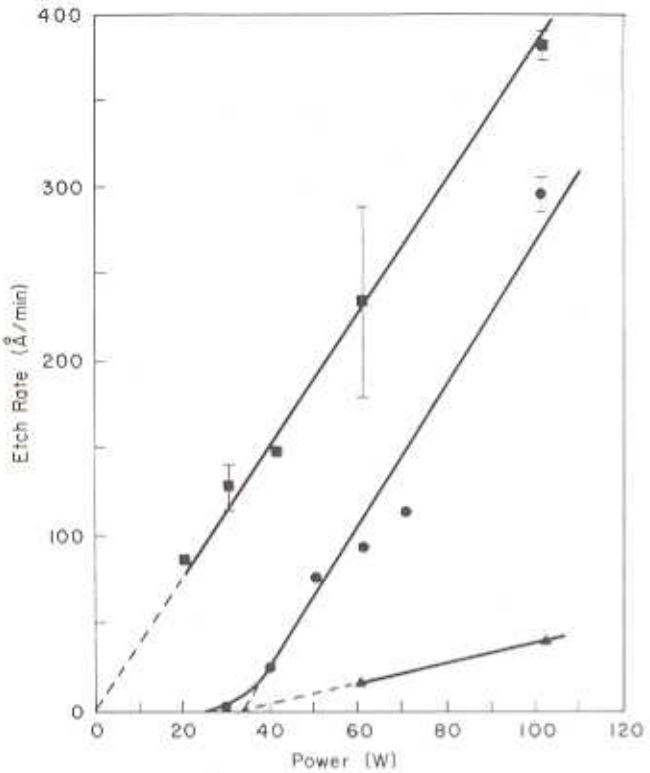

FIG. 1. Etch rate in Å/min as a function of power in watts for the resist (■) and GaAs using two different gas mixtures (100% Ar (●) and 80% Ar – 20% CF_4 (▲). The total pressure is 20 m Torr and the total flow rate is 10 sccm. The cathode is stainless steel.

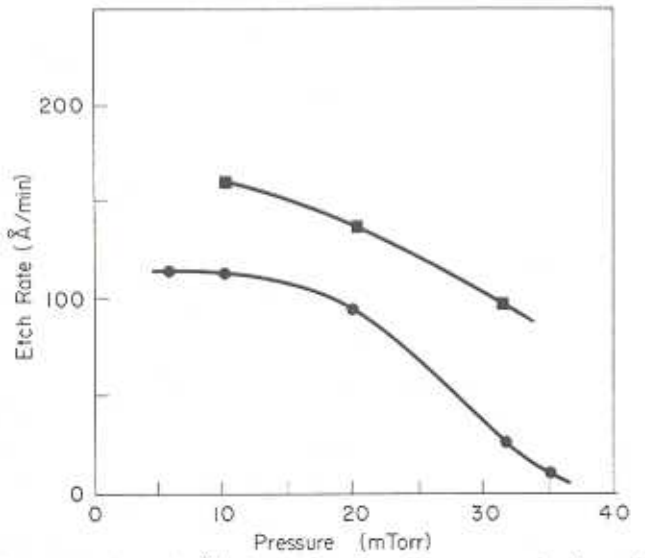

FIG. 2. Etch rate in Å/min as a function of Ar pressure for the resist (■) and GaAs (●) with a power of 100 W and a total flow rate of 10 sccm. The cathode is stainless steel.

lines show the etch rates of GaAs exposed to an inert Ar atmosphere (upper line) and GaAs exposed to a reactive atmosphere of 80% Ar and 20% CF_4. In the case of the GaAs, a power threshold of approximately 30 W is observed for both etching atmospheres. No such power threshold is observed for the resist.

We also note in Fig. 1 that the resist and GaAs etch rates for 100% Ar increase linearly, with approximately the same slope

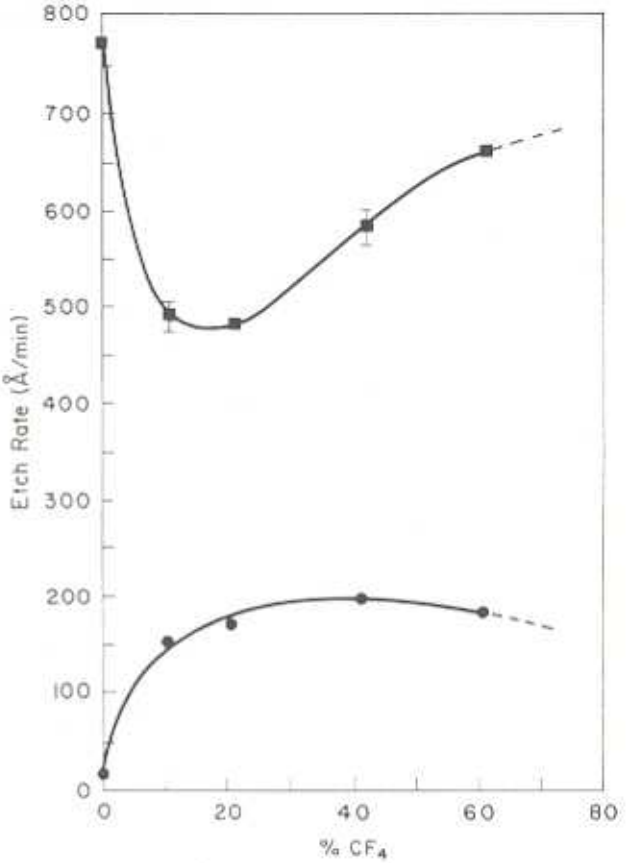

FIG. 3. Etch rate in Å/min as a function of the percentage of CF_4 in Ar for the resist (■) and GaAs (●) with a power of 100 W, a total pressure of 20 mTorr, and a total flow rate of 10 sccm. The cathode is SiO_2.

above the threshold power. This dependence can be explained by noting that as the power increases so do both the plasma ion density and the average ion kinetic energy, leading to a higher surface sputtering rate. The similar slopes of these 100% Ar lines are an indication of the common mechanical erosion mechanism by which inert gas sputtering occurs and the similarity of the binding energies of the atoms to the film surface (e.g., 2.17 eV in the case of the Ga–As bond (5)). That the resist etch rate is always higher than that of GaAs at a fixed power is a consequence of the 30 W power threshold. Finally, we notice from Fig. 1 that the GaAs etch rate for the 80% Ar – 20% CF_4 mixture is lower than that for the 100% Ar atmosphere. The reason for this is explained in Sect. 3.3. below.

3.2. Etch rate as a function of pressure

Figure 2 shows the etch rate in ångströms per minute as a function of argon pressure in milliTorr for the resist and the GaAs at a fixed applied rf power, and using an uncovered stainless steel electrode. The pressure range studied, 5–35 mTorr was limited by the performance of the MRC sputter–etcher itself. We note a decrease in the etch rate with increasing pressure for both the resist and the GaAs. This decrease is due to a decrease in the average ion energy impinging on the samples, that in turn is attributable to a decrease in both the mean free path and the observed self-bias voltage as the pressure increases. It is to be expected that at low pressure the etch rate will decrease because of the lack of ions.

TABLE 1. Surface roughness for GaAs samples etched at 100 W and 20 mTorr

Sample number	%CF_4 in Ar	Cathode	Etch rate (Å/min)	Roughness
1	0	Stainless steel	300	Rough
2	20%	Stainless steel	40	Smooth with spots
3	20%	SiO_2	175	Smooth

3.3. Etch rate as a function of CF_4 concentration

We have already noted that etch rates of GaAs samples attached to a stainless steel cathode show a sharp decrease as one adds CF_4 to the gas (8). This is due to a simultaneous deposition of a low volatility fluorocarbon layer on the top of the etched surface that prevents the etching process continuing. To avoid the formation of such a layer, a quartz disk is used to cover the stainless steel cathode (1, 5). Figure 3 shows the etch rate in ångströms per minute as a function of the percentage of CF_4 in Ar for the resist and GaAs at a fixed total pressure and using a SiO_2-covered cathode. Comparing Figs. 1 and 3 the GaAs etch rate has increased from 40 to 170 Å/min by covering the cathode with SiO_2 and using a 80%Ar–20%CF_4 mixture, at 100 W/cm^2. This is because all the reaction products of CF_4 with a SiO_2 cathode are volatile and therefore the backscattering of these products on the substrates is avoided. Reactive fluorine ions reach the GaAs surface directly and the combination of the effects of sputtering and chemical etching produces higher etch rates. We observe in Fig. 3 that the GaAs etch rate increases rapidly with the CF_4 percentage showing the positive effect of chemical etching. However, the etch rate reaches a maximum value around 40% CF_4 probably owing to the relative decrease of Ar and its sputtering. Similar behavior has been reported in the literature (1, 5).

The resist etch rate is always higher than that of the GaAs; however, the form of the resist curve is inverted relative to the curve of GaAs. The rate decreases rapidly as CF_4 is added, reaches a minimum value around 20% CF_4, and rises above 20% CF_4. This behavior can be explained if we recall that the photoresist is a polymer that can be easily decomposed in an oxygen plasma. Indeed, in a 100% Ar plasma, the silicon and oxygen of the SiO_2 cathode can be found in the plasma and can cause high etch rates. However, as CF_4 molecules are introduced, the oxygen is consumed by the CF_4 to produce CO and CO_2, thus decreasing the etch rate. The increase above 20% CF_4 could be associated with the increased presence of both fluorine ions, generated from the CF_4, and oxygen ions, produced by the etched SiO_2 cathode.

Finally, it is interesting to mention that the variation in self-bias voltage cannot explain the resist etch rate variations. For 0, 10, 20, 40, and 60% of CF_4, the negative self-bias voltages were respectively 610, 630, 670, 675, and 650 V. The GaAs etch rates better reflect this variation. This suggests that the etching of GaAs is controlled mostly by the sputtering component of the mechanism (following the self-bias voltage) while the etching of the resist is more of a chemical process (independant of the self-bias voltage).

3.4. Surface damage

By damage we refer for the purposes of this publication only to surface roughening and to the modification of the electrical properties of the surface. Table 1 shows the results of surface roughening measured by optical and scanning electron microscopes on GaAs samples etched at 100 W and 20 mTorr, for three typical sets of etching parameters. Although pure argon (sample 1) produces a high etch rate, rough surfaces are observed, thereby excluding this process from the fabrication of good devices. Sample 2 shows a smooth surface with dark spots, probably associated with the thin fluorocarbon layer deposition described earlier. This could also explain the slower etch rate that is measured when the cathode is not covered with SiO_2. For sample 3, produced with a SiO_2 cathode covering, the etched surface is very smooth. The introduction of CF_4 modifies the etching mechanism such that the sputtering-induced roughness is avoided, while the use of the SiO_2 cathode creates volatile products that prevent the deposition of a fluorocarbon layer. The best surface uniformity and vertical etch ratio for our system is obtained with 0.55 W/cm^2 of power density, 20 mTorr total pressure with 20% CF_4, and a SiO_2 covering cathode.

To explore the extent of electrical damage induced by RIE, Schottky diodes in the through-wafer sandwich geometry were fabricated. The ohmic back contacts were made by depositing Au–Ge – Ni films followed by an Au layer directly on the wafer and then performing a rapid thermal anneal. Prior to the electron beam evaporator deposition through a shadow mask of the large-area (2.5 mm^2) Ti–Au Schottky contacts, half of the samples were etched by RIE and half were etched using sulphuric and peroxide acids. The RIE conditions selected were those producing the least surface roughness: 20 mTorr, 100 W, 20% CF_4 for 45 min for a total etch depth of 7800 Å. Following the sulfuric acid etch processes on the front face of the four samples, Ti–Au Schottky contacts were deposited.

The diodes were all found to have the same ideality factor of 1.2 and the same barrier height of 0.7 eV to within 3%. The only detectable difference among the diodes was that the mean capacitance of the RIE diodes was lower by 30% than that of the acid-etched diodes. This is statistically significant as the standard deviation of the capacitance measurements performed here was 10%. The lower capacitance can be seen as being due to the contribution of a series resistance of extra surface states created by the ion bombardment during sputtering or by the presence of compounds at the surface such as gallium fluoride. A more detailed electronic state spectroscopy of the diodes resulting from these two etching processes is the subject of another study.

4. Conclusion

We have performed a systematic study of the GaAs etch rates as a function of power, pressure, CF_4 concentration, and the type of cathode. We have shown that a threshold power of 30 W exists for the GaAs etch independently of the gas mixture. The study of the CF_4–Ar gas mixture shows the necessity of using a SiO_2 disk to cover the cathode. Good vertical etch rates and smooth surfaces could be obtained for GaAs by using the following condition: 0.55 W/cm^2, 20 mTorr, 20% CF_4, and a SiO_2 cathode covering.

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