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Digital Etching of GaAs Using Alternative Incidence of Cl Radicals and Low Energy Ar Ions

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Digital etching of GaAs is successfully realized using Cl radical pulse under alternating low energy Ar ion irradiation. Etch rates are independent of Cl_2 feed time between 0.3 - 0.7 seconds. When the substrate is biased at -35 V, an etch rate which corresponds to one monoatomic layer (0.5 monolayer (ML)) per cycle is obtained. Cross-sectional etch profile when the etch rate is 0.5 ML/cycle is rectangular, without any subtrench, and is quite different from the profiles obtained for other conditions.

1. Introduction

For ultra-micro fabrication processes with atomic scale controllability, a digital processing method such as atomic layer epitaxy (ALE)[1] should be established. Most research on digital processing was concentrated on the field of thin film growth. However, to realize new device structures, *i.e.* quantum box, superatom *etc.*, development of a new technique of atomic layer etching (AL etching), by which surface atoms are etched off layer-by-layer, is required. We have demonstrated digital etching of GaAs[2,3] with an electron beam excited plasma (EBEP) system[4]. In digital etching, etchant and energetic beam alternately impinge onto the GaAs surface. In the previous study, Cl_2 molecules are used as etchant and submonolayer digital etching is achieved.[2] It is reported that Cl radicals can be more easily adsorbed on the GaAs substrates than molecular Cl_2.[5] In the present study, Cl radicals generated through high density electron injection using EBEP are used as etchants to increase the amount of adsorption of etchant and to obtain layer-by-layer controlled AL etching. This abstract describes the typical etching characteristics of digital etching of GaAs using Cl radicals.

2. Experimental

The experimental setup has been described in detail in previous reports[2-4] and is reviewed here briefly. With respect to Ar ion irradiation, EBEP allows independent control of ion energy and current with large current densities.[6] Ar gas was continuously fed both into the glow discharge column (40 sccm) and to the etching column (5.0 sccm). Cl_2 gas feed, glow discharge generation in the etching column, the open-and-close sequence of a shutter placed before the sample, and bias voltage applied to the sample are sequentially controlled by a computer-controlled sequencer. Ar gas was continuously fed into the etching column both to generate a glow discharge and to purge Cl_2 gas. Scheme of the digital etching process of the present work using Cl radicals is divided in the following four steps as shown in Fig. 1.

(1) *Etchant feed* (0.1 - 2.0 seconds): A Cl_2 gas pulse, synchronized with glow discharge plasma generation, is introduced into the etching chamber, and Cl radicals are generated. A shutter placed before the sample stage is closed and the sample

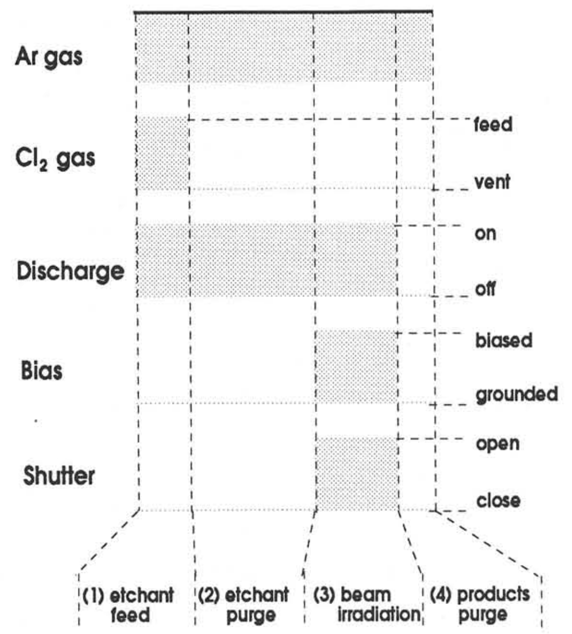

Fig. 1 Conceptual scheme of digital etching using Cl radical pulse and alternating Ar ion irradiation.

stage is biased at ground, so that no ion irradiates the surface and consequently no etching occurs at this step. Cl radicals generated in the etching chamber diffuse behind the shutter and adsorb at the GaAs surface. The Cl_2 ventilation valve is operated in inverse phase to the introduction valve and the pressure in the ventilation line is balanced with that in the etching chamber to stabilize the Cl_2 flow.

(2) *Etchant purge* (3.0 seconds): The Cl_2 introduction valve is closed and residual Cl in the etching chamber is purged. Ar glow discharge is maintained during this step to release the Cl atoms adsorbed on the chamber wall.

(3) *Beam irradiation* (2.0 seconds): By applying an appropriate bias voltage to the sample followed by the immediate opening of the shutter, Ar ions bombard the surface. The impact energy of an Ar ion is given by the differential between plasma potential and applied bias. The plasma potential with the substrate grounded was measured to be about -18 V by the single probe measurements. Although the Ar ion current was difficult to measure with the present setup (bias voltage is applied to the entire stainless steel flange attached to the sample stage), several mA/cm^2 of incident ion current is estimated from previous results.[6]

(4) *Products purge* (1.0 seconds): The discharge is turned off, the shutter is closed, and the sample is biased at ground again. During this step, all etching products are exhausted from the chamber.

Samples were (100)$\pm$0.5° oriented n-typed GaAs substrates (Si doped, 2×10^{18} cm^{-3}). Substrates were cleaned in organic solvents followed by etching in $H_2SO_4 : H_2O : H_2O_2 = 4:1:1$, and pre-sputtered by Ar ions with 110 eV of impact energy for 15 seconds. During this procedure, the GaAs sample was set on the water-cooled sample stage made from stainless steel. The temperature during etching was maintained at room temperature. The samples were masked by patterned CVD-SiO_2 films and the etch rate was determined by measuring the etched depth after 500 etching cycle.

3. Results and Discussion

Figure 2 shows the variation in etch rate as a functions of Cl_2 feed time at -35 V and -45 V applied bias voltages. Etch rates per cycle are shown

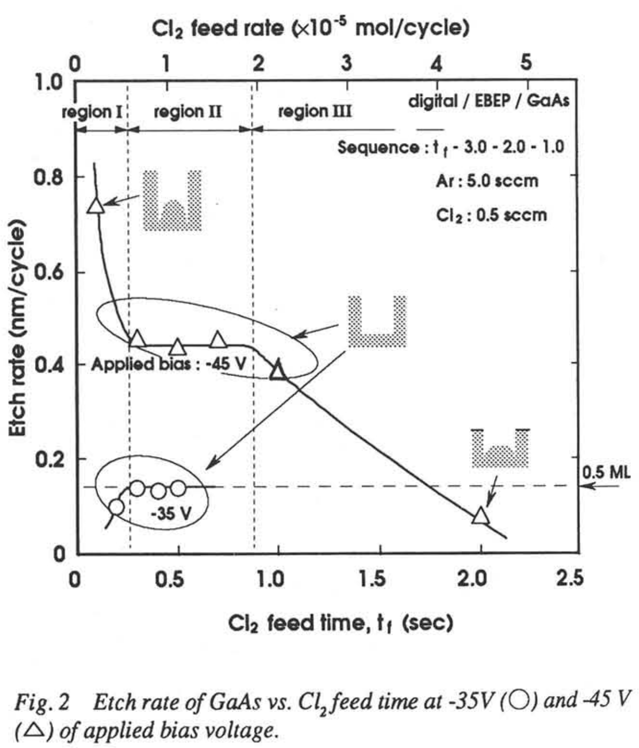

Fig. 2 Etch rate of GaAs vs. Cl_2 feed time at -35V (○) and -45 V (△) of applied bias voltage.

and the etching sequence time is inserted in the figure (in seconds). The broken line in the figure indicates an ideal etch rate equivalent to AL etching (0.5 ML per cycle). Inserted figures show schematic etched cross-sections measured by a surface profilometer. Biased at -45 V, etch rate decreases rapidly with increasing Cl_2 feed time (region I) and is constant at t_f = 0.3 - 0.7 s (region II). Excessive Cl_2 is found to cause the suppression of etch rate (region III). When a bias of -35 V is applied to the sample stage, etch rate increases in region I and is independent of Cl_2 feed time in region II. The constant etch rate at -35 V is 0.5 ML per cycle which corresponds to that of AL etching. Consequently the digital etching characteristic (etch rate is independent of certain etching parameters) is obtained in region II for the Cl_2 feed time. It is noteworthy that the etch profile in region II is rectangular and that no subtrench at the leading corners is observed.

Figure 3 shows the corresponding surface morphology after etching observed by a scanning electron microscope (SEM). Contaminations

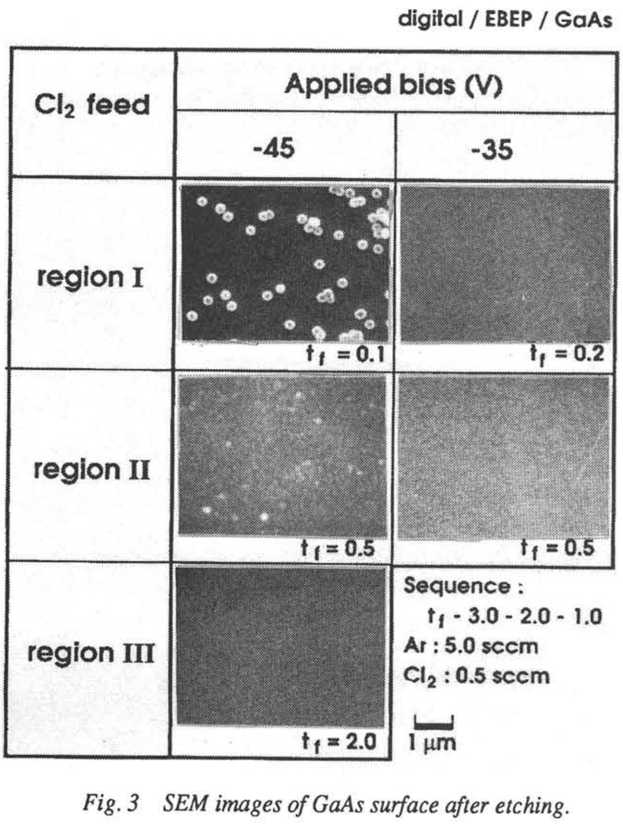

Fig. 3 SEM images of GaAs surface after etching.

are observed at the sample surface when etching is carried out with a bias voltage of -45 V. These contaminations decrease with increasing Cl_2 feed time. On the other hand, surfaces etched with biasing at -35 V are smooth and no contamination is observed.

The dependence of etch rate on Cl_2 feed time is shown in Fig. 2 is interpreted by the summation of the physical sputtering rate, the chemical sputtering rate and the passivate formation rate. Physical sputtering by direct Ar ion bombardment of the surface atoms decreases abruptly with increasing Cl_2 feed time due to the accumulation of Cl atoms on the surface. Ideal chemical sputtering increases and then saturates with Cl_2 feed time, but suppression of etching owing to the surface passivate would increase, so that the practical characteristics of chemical sputtering would have a peak or plateau at a certain Cl_2 feed time. Therefore, etch rate biased at -45 V tends to decrease with increasing Cl_2 feed time. The effect of physical sputtering can be neglected when biased at -35 V, hence the etch rate in region I increases. The constant etch rate in region II is considered to a result from the equilibrium of physical sputtering, chemical sputtering and passivate formation. Detailed consideration is being carried out and will be published elsewhere. Namely it is important to balance these contributing factors to achieve the digital characteristics. It should be pointed out that in region II the etch rate is independent of Cl_2 feed time and is equivalent with that of AL etching. In this region with a bias voltage of -35 V, pretty good surface morphology is obtained.

With alternative incidence of Cl radicals and Ar ions, excessive Cl_2 feed causes suppression of etch rate as seen in region III of Fig. 2. It has been reported that accumulation of Cl on the GaAs substrate suppresses the etching performance.[7] In the present work, arsenic chlorides are expected to be desorbed without Ar ion irradiation and gallium chlorides remain on the surface after Cl_2 feed. Excessive Cl_2 feed causes the accumulation of gallium chlorides and Cl, hence the etching performance is suppressed. It is of interest that deep trench structures at corners are observed similar to those in region I. Excess Cl_2 feed has been reported to cause the acceleration of etch rate around corners due to the formation of "liquid-like" etching compounds of $GaAsCl_8$ from $AsCl_3$, $GaCl_3$ and Cl_2.[8] At the leading corners, arsenic chlorides is not desorbed easily owing to the formation of this "liquid-like" component. It is quite probable in digital etching that "liquid-like" compounds are produced at corners due to the accumulation of chlorine and/or chlorinated compounds since the duration of etchant feed and Ar ion incidence are completely separated. Therefore a deep subtrench is formed at the leading corner.

4. Summary

In conclusion, digital etching of GaAs using pulsed Cl radicals as an etchant and alternating Ar ion bombardment is studied. By adjusting the applied bias, the etch rate becomes independent of Cl_2 feed time and is equivalent to 0.5 ML. Excess Cl_2 feed causes deposit contaminants on the surface and produces trenches at corners. Detailed mechanism and surface processes are being discussed and further study is underway, however, it should be noted that novel etching characteristics which are not seen in conventional etching methods are observed in digital etching.

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