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SELECTIVE ETCHING OF n-TYPE GaAs IN A CrO₃-HF-H₂O SYSTEM UNDER LASER ILLUMINATION

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Abstract.— A wide range of CrO₃/HF mixtures in diluted form and under laser illumination (λ = 6328 Å) have been found to be useful for defect revealing in n-type {100} GaAs. After removal of 0.2 - 0.4 microns from the GaAs surface, striations, dislocations, stacking faults and inclusions are revealed, so these etchants can be used to study defects in GaAs epitaxial layers. The characteristic features of the etch figures are similar to those obtained with the DABL method (diluted AB etch under laser ill.) but some properties of the CrO₃-HF-H₂O system are advantageous: the composition of etchants (within wide limits) is not critical for the defect revealing mode (although the kinetics of etching are composition dependent), no precipitates are formed in solution, high reproducibility of the method, no memory effect. These diluted Sirtl-like etchants used with laser (DSL) were calibrated with AB-etch and compared with the DABL method.

1. Introduction

Through the last decade much interest has been given to the development of techniques which are able to detect and to characterize the defects and homogeneity of dopant distribution in GaAs. Among them two groups of methods are most frequently used viz.: (i) anodic etching [1-4] and (ii) chemical etching with light [5-8]. The common aim of these techniques is to reveal defects and inhomogeneities with an etch depth as small as possible because of the possibility to apply the method to thin epitaxial layers. From this point of view the best methods are anodic defect revealing [4] and etching under laser illumination, the DABL method [7]. In both cases the removal of 0.2 - 0.5 μm material from the GaAs surface is adequate to delineate defects, so in this respect they can be regarded as equal. However, experimentally the latter method seems to be more attractive because of the simplicity of the equipment. A disadvantage of the DABL method is on the other hand the formation of silver containing precipitates during the mixing of the compounds (CrO₃ and AgNO₃) which brings an uncontrolled factor in the etching procedure.

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During a search in our laboratory for the most efficient and simplest method giving reproducible results in defect revealing on GaAs surfaces, it was found that also diluted Sirtl or Sirtl-like mixtures can be applied for this purpose. The Sirtl etch itself is known as a defect revealing etch for silicon [9] and there are reports for its use in undiluted form on GaAs [10,11]. This mixture does not show any ageing effects. However, the etch rate is too high to apply the method to thin epitaxial films. Therefore it seemed wise to study the Sirtl etch and Sirtl-like etchants in diluted form, with and without laser illumination, to see if they could be used as defect revealing etchants on GaAs, thereby removing only a few hundred nanometers of the crystal surface.

The aim of this paper is to describe the preliminary results of etching (100), n-type, Si-doped laser quality GaAs wafers with Diluted Sirtl-like mixtures under Laser illumination, the DSL method.

2. Experimental procedure

The GaAs substrates used in this study were n-type, silicon doped with a carrier concentration of \((1.2 \pm 2.7) \times 10^{18} \text{ cm}^{-3}\), mobility \((2.3 \pm 1.8) \times 10^{3} \text{ cm}^{2}/\text{V.s}\), resistivity \((2.2 \pm 1.2) \times 10^{-3} \text{ Qcm}\), and \((100)\) orientation of the surfaces. After conventional mechano-chemical polishing all samples were subject to the anodic dissolution method [12] in order to remove \(4 \div 5 \mu \text{m}\) of material. It is known that this procedure gives a perfect mirror-like surface. After the process an oxide layer was present on the surface which to some extent protected the surfaces from damage and dust contamination. These oxide layers were removed just before etching with a HCl+H_{2}O mixture (% 1M HCl).

The basic solution used for the experiments was the 1/1 Sirtl etch, i.e. 1 vol. part of HF standard solution (48 wt% in water) mixed with 1 vol. part of standard solution CrO_{3} (33 wt% in water). This basic solution was diluted with water within the range 1:4 to 1:40 (by volume). For some experiments the dilution ratio was settled to 1:8 and the ratio of HF/CrO_{3} standard solutions was changed within the range 0 to 5 (by volume). The thickness of the solution layer above the samples was never larger than 5 mm, so as to make sure that absorption of light by the liquid was always negligible. The etchant temperature was \(21 \pm 2\)°C. During etching the samples were illuminated by a He-Ne laser (6328 Å wavelength, power 24 mW). The optical beam width was adjusted to obtain 0.12 W/cm², the same value as used in reference 7. The GaAs wafers were partially covered with wax to enable exact measurement by a step profiler of the etch depth after the etching procedure. For calibration purposes a comparison was made with the AB etch [13] and the DABL method [7]. After etching the surface features were examined with interference microscopy.

3. Experimental results

3.1 Composition of etchant

Throughout this paper the notation \(D_{1:x}S_{a/b}\) is used for a 1:x dilution (by volume) with water of a mixture of a vol. parts HF-(48 wt% in H_{2}O) with b vol. parts CrO_{3}-(33 wt% in H_{2}O) solution.

The results of the measurements of the etching velocity as a function of the dilution of the basic 1/1 Sirtl etch are given in figure 1. It is worth noting that the surface features after etching within the whole 1:4 to 1:40 dilution range are similar in spite of the difference in etching velocity (see figures 5a, 7a-b). However, for a better control of the thickness of the layer which has to be removed, which in particular is important in the case of defect revealing in epitaxial layers, a dilution ratio greater than 1:25 is recommended.

One of the most attractive features of the CrO_{3}-HF-H_{2}O system is that neither the dilution ratio nor the ratio of HF to CrO_{3} standard solutions are critical for defect revealing. Figure 2 shows how the etching velocity depends on the ratio of HF and CrO_{3} standard solutions in the diluted Sirtl-like mixture. Over this whole investigated range of HF/CrO_{3} mixtures the defects can be discerned, however, for a ratio larger than 2/1 the surface becomes opaque, figures 3a-b illustrate this phenomenon. One sample was divided into two parts and near the common edges they were etched under...
laser illumination in 5/1 and 1/1 mixtures. Different etching times were used to remove the same amount of material. The "large" defects (dislocations, strations) can be distinguished in both cases but in case of the 5/1 mixture smaller defects like precipitates cannot be discriminated from the irregularities of the surface etch figures. The mixtures useful for high resolution defect revealing purpose were found to lie in the range of 1/5 till 1/1.

3.2 Photo etched patterns

It was proven that by a surface treatment of a GaAs wafer by the DSL method, the main defects which are present in GaAs crystals are easily revealed: growth striations, dislocations (perpendicular, parallel or inclined to the surface), stacking faults, inclusions and micro precipitates. Below they are given in more detail. Growth striations are visible after a very short etching time, i.e. after removal of 0.2 ± 0.5 μm (see figures 4a, 5a, 6a and 7a-b). Their density (spacing) depends on the dilution ratio 1:X in the etch solution with water, under laser illumination. The etching velocity of the sample changes with the ratio of HF to CrO₃ standard solutions under laser illumination. The dilution ratio of these mixtures with water is 1:8.
Fig. 3: The surface status after $D_{1:8S_1/JL}$ (a) and $D_{1:8S_5/JL}$ (b) etching of two nearby parts of the same GaAs sample. Etch depth $\sim 1 \mu$m. See text for notation.

Fig. 4: The defects on (100) GaAs surface after $D_{1:8S_1/JL}$ etching. The etch depth: (a) 0.5 $\mu$m, (b) 1.5 $\mu$m, (c) 2.5 $\mu$m, (d) 5 $\mu$m.
position of the sample in the GaAs wafer. Dislocations are shown in figures 4a-d: perpendicular to the surface marked (1) and parallel or slightly inclined to the surface marked (2) and (3). Micro precipitates are indicated by arrows in figures 4a and 4c. An important observation in these time-sequence pictures is that in case of the DSL method the "memory" effect \cite{14} does not exist, in contrary to what has been found in the AB etching system (including DABL \cite{7}). This follows from a careful examination of figures 4a-d. It can be seen that after prolonged etching: (i) a change in the geometry of defects (2) can be noticed; (ii) micro precipitates, which had been revealed after removal of 0.5 \( \mu \text{m} \) (some of them are marked with arrows in fig. 4a), disappear upon further etching (fig. 4b), while new micro cavities or groups of micro precipitates appear (see arrows on fig. 4c) and disappear again after further etching (fig. 4d).

On the other hand a memory effect does exist for the AB etch because the same defects (arrows and letter (A) on figure 5a) can be easily distinguished after prolonged etching with AB solution of the sample which had previously been treated with the DSL method (figures 5b-c). This also demonstrates that the same defects can be revealed by DSL and AB etchant.

Stacking faults (S.F.) are visible after DSL etching as straight lines lying parallel to the <110> directions, figure 6a. They are bound by dislocations (D). Both defects are inclined to the surface, which can be exposed by using the memory effect of the AB etch, figure 6b.

Finally one of the samples was divided into 3 parts, each of which was subjected to a different etching procedure in which approximately the same amount of material was removed, in order to have a direct comparison between the DSL and DABL methods; see figures 7a-c. The density of the defects and their morphology is quite similar, some differences arising from local changes between the 3 samples.

4. Conclusions

A further development in the field of a very sensitive selective etching of GaAs under illumination was made. The method is based on the Sirtl etch used in diluted form together with the illumination of a He-Ne laser (the DSL method). It was shown that a wide range of diluted Sirtl 1/1 mixtures can be successfully used for defect revealing in GaAs. Similarly, the ratio of HF to CrO\(_3\) standard solutions, within the range 1/5 to 1/1, for a given dilution ratio, is not critical for revealing the surface features after etching, but strongly influences the velocity of surface reactions. In addition it was shown that the morphology of the etch figures obtained with the DSL method is quite similar to that obtained with the DABL method. The DSL method was calibrated with conventional AB etch.

The characteristic features of the DSL method can be summarized as follows:
1) it is a simple CrO\(_3\)-HF-H\(_2\)O system, ensuring high reproducibility of the etching procedure (no ageing or precipitation);
2) small etch depths of 0.2 ± 0.4 \( \mu \text{m} \) are required for a good discrimination of striations, dislocations, stacking faults and micro precipitates on \{100\}, n-type Si-doped GaAs surfaces;
3) no memory effect occurs.
Fig. 5: The time-sequence pictures of the \{100\} GaAs surface after etching: (a) $D_{1:40^S_{1/1}}$ to an etch depth of 0.3 \(\mu\)m; (b) followed by an AB etch to an etch depth of \(\sim 10 \mu\)m; (c) again followed by a prolonged AB etch to a depth of \(\sim 20 \mu\)m.

Fig. 6: Stacking faults (S.F.) and dislocations (D) on \{100\} GaAs surface after etching: (a) $D_{1:25^S_{1/1}}$, etch depth 0.4 \(\mu\)m; (b) further AB, etch depth \(\sim 30 \mu\)m.
Fig. 7: Etch figures on (100)GaAs surface after: (a) $D_{1:25S_{1}/L}$, etch depth $\sim 0.4$ μm; (b) $D_{1:8S_{1}/L}$, etch depth $\sim 0.5$ μm; (c) $D_{1:6A_{1}L}$, etch depth $\sim 0.5$ μm.

A more complete investigation of the DSL etching systems, in which in particular more attention will be given to the chemical and physical backgrounds, is in progress and will be reported on shortly.

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