Table III. Contrast of an As particle of thickness t in a 6.9 nm thick silicon matrix. Multislice calculation, 200 kV, bright field

t	I_{max}	ΔI	C
0.8	2.57	0.028	1.09
1.2	2.57	0.040	1.55
2.4	2.57	0.064	2.50

$\Delta I = I_{\text{outside particle}} - I_{\text{inside particle}}$; $C = I/I_{max}$.

Conclusions

This work has demonstrated the formation of arsenic precipitates in silicon for both the implanted doses and the annealing temperatures investigated in our experiments. In addition to precipitation, other defects like RLD at 450°C and dislocations, loops and stacking faults at 900°C have been observed.

The arsenic content in the observed particles, assuming an SiAs composition, results to be much less than the inactive dose. Despite the presence of the other defects which could be in principle decorated by As atoms (*e.g.* RLD's, dislocations, and loops), the resulting overall As concentration is not sufficient to account for all the inactive dose. Even the segregation of As at the surface, which is known to occur, reduces but does not eliminate this discrepancy. The answer to this problem can be given by the invisibility, in the electron microscopy images, of the particles in the subnanometer range. This hypothesis is supported by computer simulation of HREM images, performed assuming particles of decreasing size. Work is now in progress to investigate in a more quantitative way the relevance of this phenomenon.

Acknowledgments

The authors are indebted to A. Parisini for the simulation of the HREM images, and to E. Gabilli, A. Garulli, D. Govoni, R. Lotti, and P. Negrini for their skillful technical assistance. This work has been partially supported by a Contract of Jumelage of the European Economic Community.

Manuscript received Feb. 28, 1986.

C. N. R. Istituto LAMEL assisted in meeting the publication costs of this article.

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A Controllable Etchant for Fabrication of GaSb Devices

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ABSTRACT

A survey of conventional etchants for GaAs shows them to be inappropriate for GaSb. The reasons for this are investigated and a novel etch for GaSb proposed. This etchant, consisting of HCl/H_2O_2/NaK (tartrate) solutions, gives controllable etch rates from 0.1 to 2.0 μm min^{-1}. Smooth surfaces free from etch pits and surface films are obtained.

The alloy AlGaAsSb is potentially a suitable material for optical devices in the preferred spectral region 1.3-1.7 μm (1-3). Recent advances in the epitaxial growth of this material suggest that it will shortly become of some technological importance (4-6). If such devices are to be realized, a controllable etchant system for compounds containing Sb is required. Examination of the literature reveals little systematic study of etchants suitable for the fabrication of devices based on GaSb.

Experimental

The substrates were Bridgman grown GaSb (001) doped with Te or Zn. These were coated with 2.1 μm photoresist (AZ1350J) and stripes of 50 and 20 μm width defined in the

Table I.

Etchant	Action
HCl or $H_2SO_4/H_2O_2/H_2O$	Inactive due to formation of passivating film
HNO_3/H_2O	Violent reaction
KOH or $NH_3/H_2O_2/H_2O$	Inactive

(110) and $(1\bar{1}0)$ directions. The substrates were then mounted on glass slides and exposed to freshly prepared etchant solution for 2 min with manual agitation of the solution every 15s. The etch was quenched in water. After removal of the photoresist the depth of the etched step was measured with a dektak and the surfaces examined by optical and scanning electron microscopy.

Results and Discussion

A survey of conventional etchants from GaAs technology showed them to be inappropriate for GaSb (Table I).

The mechanism of wet chemical etching consists of two distinct steps: (*i*) oxidation of the surface layer, and (*ii*) dissolution of the resulting oxidized species. Failure of the second step leads to a buildup of a passivating oxide layer. Observation of a yellow film when GaSb was exposed to acid/H_2O_2 solutions suggests that etching fails due to buildup of Sb_2O_5, a yellow solid known to be insoluble in aqueous acid or alkali (7). By contrast, As_2O_5 is soluble in aqueous media—hence the effectiveness of these etchants for GaAs.

This observation suggests that etching might be achieved in the presence of some complexing agent that renders the oxidized Sb soluble. Several soluble compounds of Sb(V) exist, including two containing the tartrate ion $[C_6H_4O_6]^{2-}$. An investigation of etching by solutions of HCl/H_2O_2/NaK (tartrate) was therefore undertaken.

Figure 1 shows the dependence of etch rate on the molar concentration of H_2O_2 ($[H_2O_2]$) at two concentrations of tartrate ion ([tartrate]). This figure illustrates the two steps at which kinetic control of etch rate may occur. For low [tartrate] (83 m*M*) and at low $[H_2O_2]$ (up to 700 m*M*), the rate is controlled by the oxidation step and the reaction rate is proportional to $[H_2O_2]$. At high $[H_2O_2]$ (>700 m*M*), the etch rate is controlled by the dissolution step and becomes independent of $[H_2O_2]$. This is confirmed by the observation of oxide films under these conditions. Increasing [tartrate] to 167 m*M* increases the rate of the

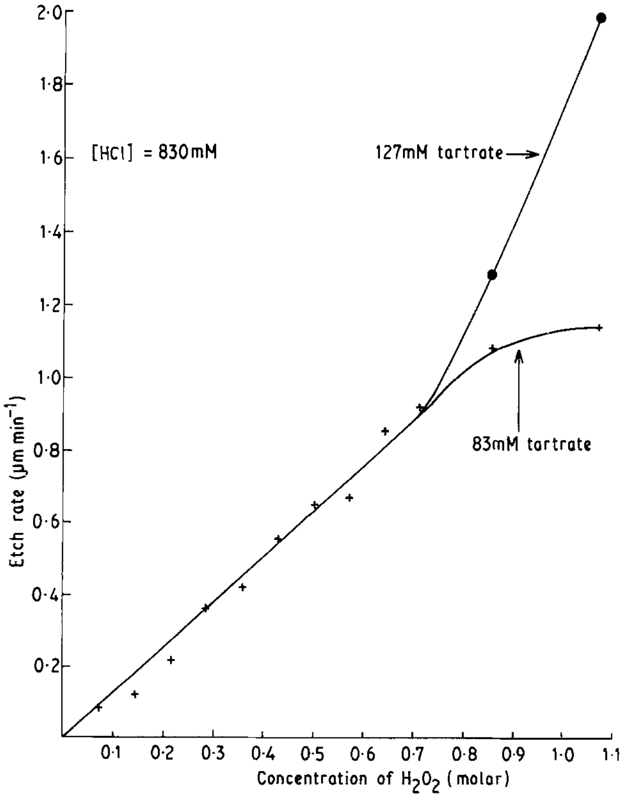

Fig. 1. Variation of etch rate with concentration of H_2O_2 for two concentrations of tartrate.

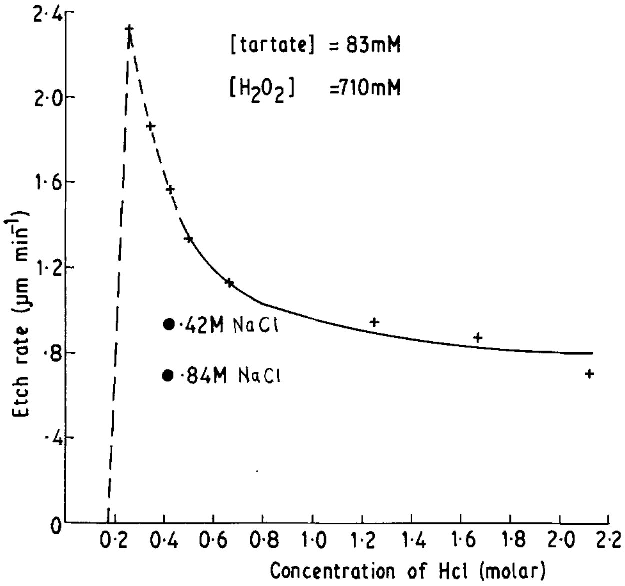

Fig. 2. Variation of etch rate with concentration of HCl and NaCl

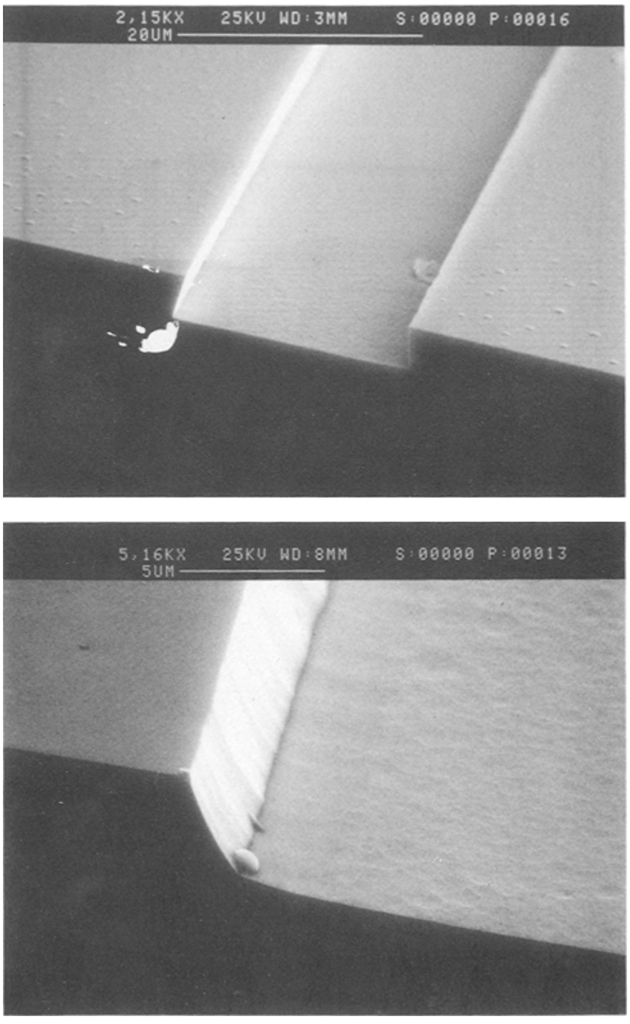

Fig. 3. 20 μm wide stripes etched in GaSb: (a, top) (110) orientation; (b, bottom) $(1\bar{1}0)$ orientation.

dissolution step, and the etch rate becomes dependent on [H_2O_2]. The use of very high [H_2O_2] (>1200 m*M*) leads to uneven etching. The reproducibility of these etch rates is strongly dependent on control of the agitation of the solution. The etch rate increases with more frequent agitation. This suggests that the etch rate is controlled by diffusion of the reagents to the substrate surface. Under carefully controlled conditions (one "swirl" every 15s), etch rates could be controlled to ±10%.

Figure 2 illustrates the dependence of etch rate on HCl concentration ([HCl]). No etching is observed for very low [HCl] due to buffering of the solution by the tartrate ion. Above a threshold of [HCl] = 200 m*M*, the etch rate rises to a maximum of 2.3 μm min^{-1} but then falls with increasing [HCl]. This fall in etch rate appears to be a result of the increased chloride ion concentration, since it can be reproduced by addition of NaCl to the reaction mixture (Fig. 2), whereas addition of $NaBF_4$ actually increases the etch rate. The origin of this effect is thought to lie in the complex effect of different ions on diffusion rates in aqueous media.

Figures 3a and b show electron micrographs of etched stripes in the (110) and ($1\bar{1}0$) directions, respectively. Undercutting is observed in Fig. 3a and a mesa shape in Fig. 3b, indicating the orientation of the stripes (8). It is clear from these micrographs that the etched surfaces are smooth and free from etch pits.

Conclusion

The etchant system HCl/H_2O_2/Na K (tartrate) gives controllable etch rates from 0.1 to 2.0 μm min^{-1}. Smooth surfaces free from etch pits, and surface films are obtained.

Acknowledgments

This work was partially supported by the Joint Optoelectronics Research Scheme and partially supported by Central Funds.

Manuscript received June 9, 1986.

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Reaction Mechanism of GaAs Vapor-Phase Epitaxy

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ABSTRACT

Reaction mechanisms of GaAs epitaxial growth using GaAs-$AsCl_3$-H_2 and GaAs-$AsCl_3$-N_2 systems have been investigated by means of infrared spectroscopy, and probable reaction models are discussed. Over the whole temperature range of 400° ~ 840°C, dominant gallium chlorides observed by a sampling method are Ga_2Cl_6 and an unidentified gallium compound with chlorine that has an absorption band at 1600 cm^{-1} in the hydrogen carrier system, but only Ga_2Cl_6 in the nitrogen carrier system. Analyses by a mechanical balance have suggested that $GaCl_3$ sampled from a reactor should dimerize into the greater part of Ga_2Cl_6 in a gas cell. A photoenhancement of $AsCl_3$ reduction by H_2 has been examined by irradiating with an excimer laser. A photoexcitation of $GaCl_3$ has been ascertained, and epitaxial growth with a single flat temperature profile has been realized at low temperatures below 600°C by irradiation with a 249 nm laser.

The preparation of highly perfect epitaxial layers whose thickness is controlled to a single atomic dimension is necessary for the fabrication of extremely high speed devices, ultrahigh frequency devices with a hyperabrupt doping profile, and optoelectronic devices of a high quantum efficiency. III-V compound semiconductors have such an essential problem that a deviation from the stoichiometry occurs easily at high temperatures (1). Since nonstoichiometric defects badly affect basic properties of those devices, development of low temperature processes is quite urgent. Low temperature processes would be classified into two groups; plasma process (2) and photoexcited process. One of the authors (J. Nishizawa) proposed photoexcited process in 1961 (3) and extended its use to the vapor-phase epitaxial growth of Si and GaAs (4-6). Through those studies, it has been shown that irradiation of UV light onto the substrate provides both the improvement of crystal quality and the enhancement of growth rate at low temperatures. Moreover, the author combined this photoexcitation technique with GaAs molecular layer epitaxy to realize single crystalline film growth at a substrate temperature as low as 350°C (7).

In order to derive full advantage of such advanced growth techniques as photoexcited epitaxy, molecular layer epitaxy, etc., and to keep them in an optimum control, it is necessary to understand the mechanism of crystal growth from the vapor phase. A layer growth mechanism dominated by surface migration of adsorbed clusters was proposed for the vapor-solid phase interaction (8-10), but the reaction process in the vapor phase has not been clarified yet, especially in the GaAs epitaxial growth. Besides an early work by Shaw (11), a number of models of vapor-phase reactions and transport phenomena in GaAs epitaxial growth were deduced mostly from an equilibrium viewpoint (12-14). Actual reactions, however, are not necessarily in equilibrium. Therefore, an essential premise to the understanding of GaAs vapor-phase epitaxy is *in situ* analysis of the gas in a reactor.

On the basis of above considerations, we have investigated the reaction mechanism of GaAs epitaxial growth using the halogen transport method by means of infrared absorption spectroscopy, which has an inherent advantage in its use of low energy light source providing no extra excitation of molecules, compared with Raman spectroscopy (15) and mass spectroscopy (16, 17). And so it was already applied to the analysis of Si and GaAs vapor-phase epitaxial growth (18, 19) and plasma etching (20). This paper describes the results of basic investigation about the reaction mechanism of GaAs vapor-phase epitaxy using the halide transport method and also about photoexcitation effects on the reactions.

Experimental

The gas analysis by infrared absorption spectroscopy was carried out in the halogen transport system using $AsCl_3$. A schematic diagram of the experimental apparatus

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