Epitaxial Growth of Mirror Smooth Ge on GaAs and Ge by the Low Temperature GeI_2 Disproportionation Reaction

M. Berkenblit,* A. Reisman,* and T. B. Light

IBM Watson Research Center, Yorktown Heights, New York

ABSTRACT

Ge epitaxial layers were grown by the GeI_2 disproportionation reaction at 350°C on (110) semi-insulating GaAs and Ge substrates. The epitaxial surfaces are comparable in quality to those obtained by the higher temperature hydrogen reduction of $GeCl_4$ on Ge substrates. Modifications of previously reported apparatus and growing conditions which lead to the enhanced surface qualities are described. These modifications include an increase in average linear gas stream velocity and GeI_2 concentrations, improved substrate surface preparation techniques, and the protection of the wafer surface from spurious nucleation during the growth process.

There has been considerable recent interest in the use of planar Ge for ultra high performance switching circuit applications at these laboratories as well as for other device applications elsewhere. Ge grown on semi-insulating GaAs is being investigated as a starting material for an alternate, improved approach to device isolation over the presently employed junction isolation schemes. The Ge/GaAs system is potentially useful because of the apparent close structural match of the two materials, the semi-insulating properties of Cr doped GaAs, and the retention of these insulating properties during low temperature Ge deposition processes and subsequent device fabrication steps.

Among the potential methods for the deposition of Ge on GaAs (*i.e.*, pyrolytic reduction of the tetrahalide, decomposition of GeH_4, and the dihalide disproportionation reaction) the GeI_2 disproportionation reaction is attractive because of the associated low temperatures. Notably, low temperature reactions have led in the past to poor surface qualities when compared to higher temperature processes. In addition, the surface characteristics showed a marked dependency on substrate orientation (1, 2).

This paper describes a method by which n- and p-type Ge epitaxial layers may be grown via the iodine process at a substrate temperature of 350°C on (110) semi-insulating GaAs and Ge substrates. The grown surfaces are mirror smooth and shiny, and are comparable to those obtained by the higher temperature hydrogen reduction of $GeCl_4$ on Ge substrates. Changes in deposition parameters, improved substrate preparation and modifications of the apparatus previously reported on (2) are described which have led to the enhanced surface qualities. Of note also, is the fact that growth rates using the new procedure are comparable to those obtained in higher temperature epitaxial growth techniques.

Experimental Procedure

Flow and temperature.—The Ge layers were grown in a horizontal system with a 1 in. diameter deposition chamber. The pertinent thermodynamics and basic flow system have been described earlier by the authors (2-4). The substrates were maintained at a temperature of 350°-355°C and the Ge source bed was held at 600°-620°C. A 15% H_2-85% He mixture was used as a carrier gas at an input flow rate of 915 cc/min which, expressed as a room temperature linear gas stream velocity at the substrate, is 190 cm/min. The I_2 source for the HI generator was maintained at 65°-75°C (±0.2°C at a given temperature) which encompasses a range of HI pressures of 11.0-20.5 Torr.

* Electrochemical Society Active Member.

Reagents.—The carrier gas was mixed in the system (Matheson ultra pure H_2 and He). Traces of O_2 and H_2O were removed by passing this mixture through a heated Pt bed (450°C) in series with a liquid nitrogen freeze out trap. The HI generator used was the modified version described in ref. (5).

The Ge source material was Eagle-Picher intrinsic grade (40 ohm-cm or better). In order to extend the time between reloading Ge charges, a larger source bed was constructed to replace the one employed in the previously reported system. This new design also offers a more efficient reaction path through the crushed Ge to accommodate the higher flows employed in the present work. As shown in Fig. 1 the source bed was made up of a number of interconnected chambers in a 1 in. diameter tube. The openings in each chamber were positioned in such a way as to insure passage of the gas through the crushed Ge.

GaAs wafers were prepared both from Monsanto (horizontal Bridgeman) Cr doped and from Czochralski pulled Cr doped single crystals grown by S. Blum of our laboratories. Ge substrates, which were used as controls, were obtained from Czochralski pulled single crystals grown in house by C. Lent. Both the GaAs and Ge bulk single crystals were oriented to within 0.5° of the (110), sliced, lapped, and then polished using the NaOCl method of Reisman and Rohr (6). In the case of p-type Ge substrates, electropolishing in a KOH solution was used to assess effects of polishing on subsequent deposits. None were noted.

Additional surface preparation.—It was found that in order to obtain mirror smooth epitaxial deposits, both the GaAs and Ge wafers, after polishing and storage, required an additional chemical treatment immediately prior to being loaded into the epitaxial reactor. GaAs wafers were treated in a solution of $90H_2SO_4{:}5H_2O_2{:}5H_2O$ (7, 8) in a hanging basket arrangement as shown in Fig. 2. The substrates were suspended in the solution in the basket, and stirring was effected via a rotating magnetic bar. The basket consists of a shallow quartz dish supported by rods and permits the cleaned wafer to be water quenched in

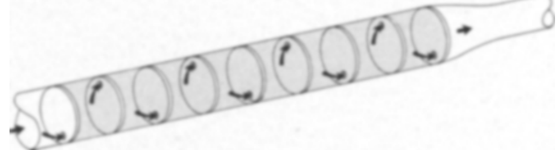

Fig. 1. Germanium source bed

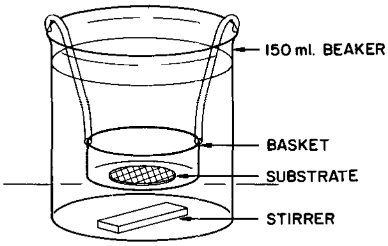

Fig. 2. Hanging basket used for cleaning GaAs substrates

situ immediately following the chemical treatment. A marked difference in surface texture was observed with different methods of agitation. For example, a pronounced degradation in the form of an orange peel texture results with the use of ultrasonic agitation in place of the method described.

Ge substrates, however, could be cleaned satisfactorily by a 90 sec treatment in a 3:1 solution of H_2O: NaOCl stock solution (5% available chlorine) using ultrasonic agitation. A final degree of surface cleaning was achieved by heating both the Ge and GaAs substrates, in situ, in a H_2 ambient for 30 min (600°C for GaAs and 700°C for Ge) prior to deposition.

One further factor that markedly affected deposit quality is the method employed for drying the substrates following chemical treatment and rinsing. If done improperly, it will invariably result in an epitaxial deposit marred by many surface imperfections. A precedure that yielded good results consistently is as follows. After chemical treatment, and quenching the chemical action in deionized water, the wafer is transferred from the etching basket to a vacuum chuck. During this transfer procedure a stream of deionized water is played on the wafer surface to prevent partial drying of the wafer. Simultaneously, the hosing action is stopped and a jet of high pressure clean nitrogen is directed onto the wafer surface to roll the water off. This enables almost instantaneous removal of liquid from the surface with a minimum amount of evaporation being permitted to take place. An example of the effects of a poor drying technique is shown in Fig. 3. In this case water was allowed to ball to the center of the substrate resulting in some drying of the edges before the surface was completely dried. Both photographs show the sharp difference in density of surface contamination. A grown layer on such a surface clearly replicates the two distinctly different areas.

Vacuum chuck substrate holder.—Previously, epitaxially deposited films were subject to the formation of large spurious overgrowths or "spikes" during the deposition process. Spikes as high as 20-30μ were observed on 5μ thick deposits when the substrates were placed face up in the horizontal deposition chamber. Because deposition in a disproportionation growth process is not confined to the substrate, but occurs on the walls of the reactor also, minute particles can flake off and serve as nuclei for these coarse protrusions. To eliminate the problem of dusting from the walls of the reactor and the attendant growth of spikes, a vacuum chuck was used to hold the substrate face down in the gas stream. The wafer holder, shown in Fig. 4, consists of a semicylindrical quartz piece and a support tube extending out of the system

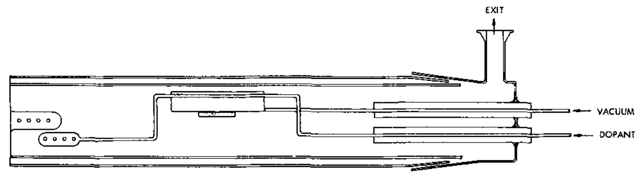

Fig. 4. Deposition chamber showing the position of vacuum chuck and dopant line.

to a vacuum line. The flat face is lapped and has a 25 mil vacuum orifice.

Doping.—Both n- and p-type Ge layers were grown using AsH_3 and BI_3, respectively, as the dopant sources. The impurities were introduced into the system through a separate gas line as shown in Fig. 4.

Experimental Results

In our earlier work, the low temperature HI-Ge vapor transport system was used at relatively low linear gas stream velocities (l.g.s.v.) and low hydrogen iodide vapor pressures (15-30 cm/min and HI in the range of 2-4 Torr). Velocities and concentrations were chosen so that the source was maintained at equilibrium, and deposition was in a quasi equilibrium or mass transport limited condition. Growth rates were in the range of 0.3-0.8 μ/hr. The epitaxial films on (110) surfaces had a dull matte appearance that was unsuitable for application of small dimension photomasking techniques. Deposits, exhibiting improved but still inadequate surface characteristics, were grown under these low growth rate conditions on several orientations other than the (110). The best surfaces under these conditions were obtained on wafers that were cut 25° off (100)→(110).

The first significant improvement in surface quality of deposits on (110) substrates was obtained by increasing both the l.g.s.v. and simultaneously increasing the vapor phase concentration of GeI_2. (As a matter of convenience the concentrations are expressed in terms of HI vapor pressures or temperature of the iodine source bed.) Attending these changes, the growth rate increased to a value ranging between 5 and 10 μ/hr depending on the exact conditions of the experiment. This increase in growth rate was, however, less than would have been predicted theoretically (3) indicating a lowered efficiency of deposition. For example, the set of conditions leading to a 10 μ/hr growth rate should have yielded a value of 18 μ/hr. Such a result is not unexpected since with increasing l.g.s.v. and gas phase reactant concentration the deposition tends to become surface limited in the manner described by the authors (5). The improvement of surface smoothness coincident with changing the growth parameters in the direction of a surface rather than a mass transport regime is in clear distinction to observations made by Silvestri for hydrogen reduction of $GeCl_4$ (9). In such a system he found that enhanced surface smoothness was directly related to maintaining the deposition in a mass transport controlled regime.

A range of operating conditions were determined which were suitable for obtaining mirror smooth surfaces. At a constant GeI_2 concentration (11.0 Torr HI), depositions were of excellent quality in the l.g.s.v. range from 95 to 190 cm/min. No experiments were

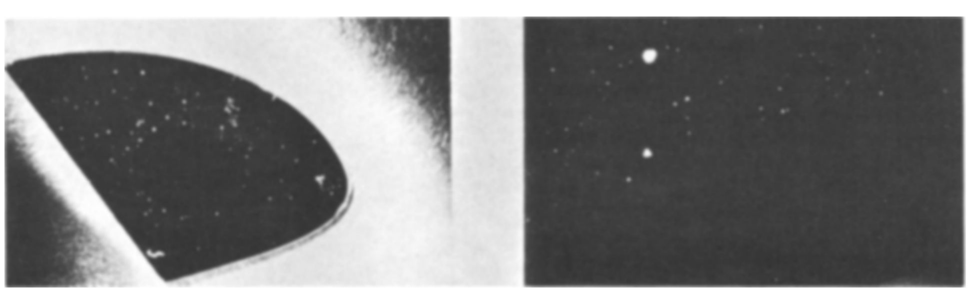

Fig. 3. Example of poor drying technique.

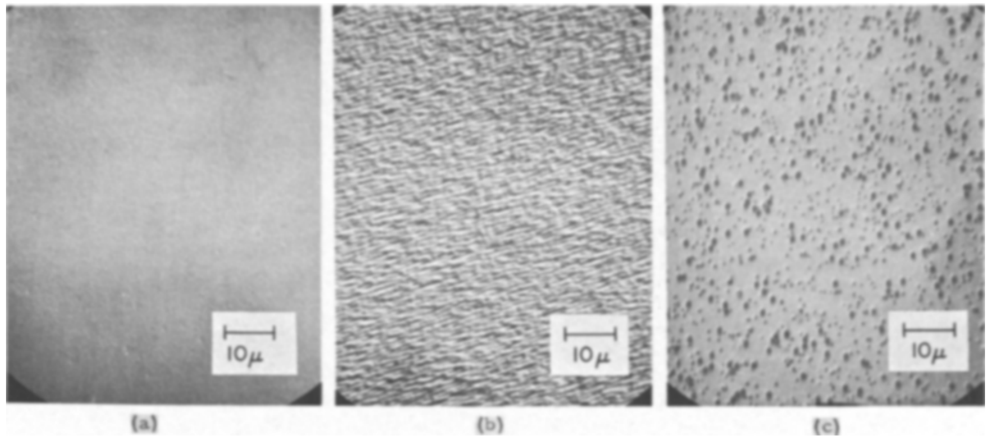

Fig. 5(a, left). Surface obtained using full process; (b, center). surface obtained without pretreatment of substrate; (c, right). surface obtained using low l.g.s.v. and low GeI_2 concentration.

conducted above 190 cm/min, and it was observed that at 50 cm/min surface quality had already degraded noticeably. At a constant velocity of 190 cm/min, smooth and shiny surfaces were obtained with HI pressures ranging between 5 and 35 Torr. Using HI pressures in the range 35 to 50 Torr resulted in visually mirror smooth surfaces which exhibited microscopic etch structures. The etching phenomenon at these higher HI pressures is believed to be due to incomplete equilibration at the Ge source.

In order to demonstrate the necessity for the several cleaning and growth condition steps described above, a series of 5μ layers of Ge were deposited on (110) semi-insulating GaAs. The three cases presented for comparison essentially summarize the over-all process. Figure 5a shows a surface obtained using the full process. Figure 5b is a micrograph of a deposit using all the critical procedures except that the substrate was not chemically treated prior to loading into the reactor. The deposit shown in Fig. 5c was obtained on a substrate which had the full cleaning procedure, but where both low l.g.s.v. and GeI_2 concentration were employed for deposition. As is evident, only the surface obtained by employing all of the critical steps is shiny and smooth. The others vary in texture from hazy to dull matte.

Stacking faults were not observed either by interference contrast microscopy or by x-ray topography. In addition, the crystal perfection of the as-grown layers were equal to that of the starting substrate as determined by the x-ray crystallographic technique of Cole and Stemple (10).

Once conditions were established for obtaining reproducibly good Ge layers, the behavior of these layers in subsequent heating cycles (*i.e.*, oxide deposition, diffusions) was examined. Ge deposits on GaAs substrates show signs of plastic deformation after heating to 500°C or higher. This behavior is attributed to strain due to a mismatch in the thermal coefficients of expansions between the GaAs substrates and the Ge epitaxial layers. Strain relief then occurs along slip planes during the heating cycle. An example of such slip line formation is shown in Fig. 6. As-grown layers were slip free, Fig. 5a.

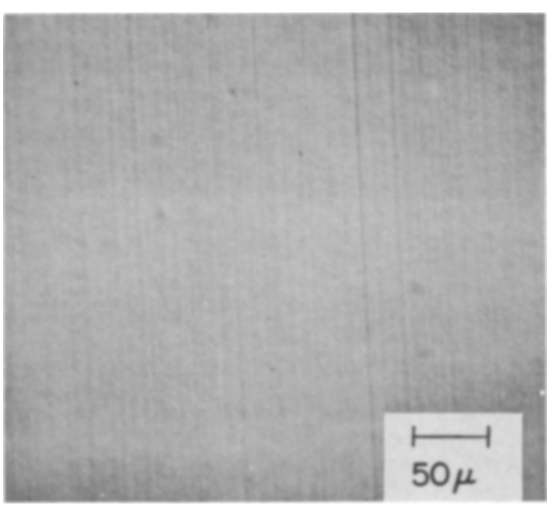

Fig. 6. Example of slip line formation

Plastic deformation was not observed in Ge grown on Ge substrates, nor would it be expected if the strain is due to a thermal expansion mismatch. Ge grown on GaAs by the pyrolysis of GeH_4 at 650°C, as reported by Reisman and Papazian (11), shows slip line formation after the initial deposition heat cycle.

Annealing or slow heat cycling did not appreciably change the extent of plastic deformation. A much thicker Ge deposit (33μ), than normally grown (5-10μ), shows the minimum decrease in crystal perfection after heating to above 500°C. The use of thin substrates (< 5 mils) prevented slip line formation because the strain relief in such a structure occurs by elastic bending of the substrate.

A complete discussion of the plastic deformation characteristics of the epitaxial films and a calculation of the stress and extent of the thermal mismatch is discussed by the authors in a separate paper (12).

In an attempt to extend the usefulness of the deposition process, several experiments were performed on orientations other than (110). It was found that the growth conditions which provided mirror smooth deposits on (110) surfaces yielded structured surfaces on (111) and (100) oriented substrates. Since our interest at the present time is confined to (110) surfaces in conjunction with their use in fabricating Post Alloy Diffused transistors (13), no attempt was made to define growth parameters applicable to other orientations.

The Ge layers deposited in the undoped state were all n-type having a carrier concentration of the order of mid 10^{14} to low 10^{15}/cc. The preparation of more heavily doped n-type material is readily achieved with use of AsH_3 as an arsenic source. The decomposition of AsH_3 occurs at the growth temperatures employed and the addition of AsH_3 to the vapor phase did not perturb the deposition process.

The use of B_2H_6 as a p-type dopant source is standard in the high temperature $GeCl_4$ process and was examined in the disproportionation growth. B_2H_6 was found usable in obtaining deposits with resistivities varying between 1-0.005 ohm-cm under low growth rate conditions. However, at the growth rates arrived at for the present work, B addition via B_2H_6 presented a problem. The maximum doping achieved was 0.02 ohm-cm and with further increase in B_2H_6 concentrations the surface quality of the epitaxial deposits degraded.

At the low temperatures of the disproportionation reaction, the incorporation of B into the growing layer is assumed to occur via an intermediate formation of BI_3 by the reaction of B_2H_6 with HI (14, 15) in the gas stream. The BI_3 yield is limited by the HI available in the gas stream and the efficiency of the reaction at the temperature of the epitaxial reactor. Therefore, in order to produce the necessary BI_3 concentrations a large excess of B_2H_6 is required which in turn perturbs the epitaxial reaction. To eliminate the dependence on this reaction, a source of BI_3 was substituted for the B_2H_6. A range of concentrations were then obtained, sufficient for all doping levels required, by passing He or H_2-He mixtures at varying flow rates through a bed of solid BI_3 maintained at room temperature. In the range of operation there was no degradation in surface quality with increasing BI_3 concentrations.

Impurity concentration profiles were not measured. However, samples of Ge grown with high and low B concentrations on semi-insulating GaAs were angle lapped. Traveling hot probe measurements did not indicate the presence of any n-type regions near the interface. This implies a negligible back etching reaction. In addition, after etching the Ge deposit away, there was no measurable degradation of the insulating properties of the substrate material.

Summary

A low temperature process for the deposition of smooth and shiny Ge epitaxial layers at 350°C has been evolved. Each of the process steps are important and are necessary for good surfaces. These process steps include: (*I*) Chemical treatment to clean surfaces. (*II*) Rinsing and drying with care to avoid evaporative drying. (*III*) Holding the wafer in an upside down position during growth, to prevent dusting and attendant spike formation. (*IV*) GeI_2 concentrations, expressed in terms of HI pressure, in the range 5-35 Torr. (*V*) Linear gas stream velocities, referred to room temperature, greater than 50 cm/min.

Acknowledgments

The authors wish to thank M. Sampogna for his assistance with the epitaxial reactor, and R. L. Rohr, J. A. Petriello, and C. X. Duncombe for the polished substrates, and J. Angilello for the x-ray work.

Manuscript submitted Feb. 2, 1968; revised manuscript received *ca.* May 8, 1968. This paper was presented at the Chicago Meeting, Oct. 15-19, 1967, as Paper 160.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1969 JOURNAL.

REFERENCES

1. J. C. Marinace, *IBM J. Res. & Dev.*, **4**, 248 (1960).
2. A. Reisman and M. Berkenblit, *This Journal*, **112**, 315 (1965).
3. A. Reisman and S. A. (Alyanakyan) Papazian, *ibid.*, **111**, 1154 (1964).
4. A. Reisman, M. Berkenblit, and S. A. (Alyanakyan) Papazian, *ibid.*, **112**, 241 (1965).
5. A. Reisman and M. Berkenblit, *ibid.*, **113**, 147 (1966).
6. A. Reisman and R. L. Rohr, *ibid.*, **111**, 1425 (1964).
7. M. V. Sullivan and L. A. Pompliano, *ibid.*, **108**, 60C (1961).
8. R. K. Willardson and H. L. Goering, "Compound Semiconductors," Vol. 1. "Preparation of III-V Compounds," Reinhold Publishing Corp. (1962); J. W. Faust, Jr., "Etching of the III-V Intermetallic Compounds."
9. V. J. Silvestri, Presented at the Chicago Meeting, Oct. 16-18, 1967, Abstract 163.
10. H. Cole and N. R. Stemple, *J. Appl. Phys.*, **33**, 227 (1962).
11. S. A. Papazian and A. Reisman, Presented at the Chicago Meeting, Oct. 16-18, 1967, Abstract 159.
12. T. B. Light, M. Berkenblit, and A. Reisman, *This Journal*, **115**, 969 (1968).
13. H. N. Yu and F. H. Dill, Presented at the Washington, D. C. IEEE Meeting, Oct. 18-20, 1967, Abstract 26.4.
14. A. E. Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press (1933).
15. R. M. Adams, "Boron Metallo-Boron Compounds and Boranes," John Wiley & Sons, New York (1964).

Plastic Deformation in Epitaxial Ge Layers Grown on Single Crystal Semi-Insulating GaAs

T. B. Light, M. Berkenblit,* and A. Reisman*

IBM Watson Research Center, Yorktown Heights, New York

ABSTRACT

The compatibility of Ge and GaAs, in terms of their temperature dependent mechanical properties, is described in this paper. Examination at room temperature of epitaxial Ge layers grown on wafers of single crystal, semi-insulating GaAs, at substrate temperatures of 700°C by pyrolytic dissociation of GeH_4, reveals evidence of plastic deformation immediately following the epitaxial deposition process. Plastic deformation is observed in epitaxial Ge layers grown at 350°C, by disproportionation of GeI_2, only after a subsequent annealing cycle to at least 500°C. The low substrate temperature Ge films, however, show elastic bending of thin substrates after deposition and cooling to room temperature. Based on these observations, it is possible to estimate the differential thermal expansion coefficient between Ge and GaAs ($1 \times 10^{-6}/°C$), and to use this result to estimate the critical shear stress for plastic deformation under low strain rate conditions (6.7×10^7 dynes/cm^2). Interface dislocations are not observed.

The present work was prompted by observations made during the course of the work described by Papazian and Reisman (1), and by the present authors (2). Plastic deformation of the Ge epitaxial layers grown on semi-insulating GaAs substrates was observed. This observation seemed inconsistent with the considerations that have motivated much work with the Ge/GaAs hetero-epitaxial system. These considerations, which were discussed by Amick (3) are: (*i*) same

* Electrochemical Society Active Member.