Chemical dissolution of indium arsenide in the Br$_2$-HBr solutions

Z.F.Tomashik, S.G.Danylenko, V.N.Tomashik, M.Yu.Kravetski
Institute of Semiconductor Physics, NAS of Ukraine,
41, prospekt Nauki, 03028 Kyiv, Ukraine, Tel.: (38044) 2655755

Abstract. The nature and kinetics of InAs chemical dissolution and chemical cutting, in the bromine solutions in hydrobromic acid have been investigated. It was shown that at low (up to 6 vol.%) bromine concentrations the InAs dissolution rate grows linearly with bromine concentration. Such solutions may be used to chemically polish InAs. Solutions containing from 20 to 30 vol.% Br$_2$ in HBr dissolve InAs with the rate 25 to 50 μ/min forming polished surfaces with etch pits. Such solutions may be used to chemically cut indium arsenide.

Key words: dissolution, hydrobromic acid, etchant, indium arsenide, bromine, diffusion stage.

1. Introduction

The etchant containing elemental bromine are widely used to etch III-V semiconductor compounds and solid solutions based on them. Such compounds are rather easily oxidized with bromine, yielding products that readily dissolve in a number of solvents. The great bulk of bromine-containing etchants belong to the polishing ones. This means that etching rate for them is determined by diffusion stages of a heterogeneous chemical reaction.

Bromine solutions in organic solvents are most often used as bromine-containing etchants. According to [1], the best results when performing polishing etching of InSb can be achieved with those etchants where methanol, dimethylsulfoxide, dimethylformamide, ethylene glycol serve as solvents. During the technological procedures aimed at semiconductor surface preparation the solutions of bromine in methanol are used rather advantageously [2-6]. It is suggested that indium, arsenic and antimony pass into solution as methoxybromides, and the reaction between InAs and Br$_2$ is of the first order in oxidant in the methanol-tetrachloride of carbon solution [2]. The rate of InP, InAs and GaAs etching grows linearly with bromine concentration at bromine content in methanol up to 6 vol.% [3]. Both the dissolution rate and sample surface quality after etching highly depend on Br$_2$ concentration in solution. For InAs the polishing concentrations of Br$_2$ in CH$_3$OH lie within the 1.5 to 2 vol.% range. Stirring of solution considerably affects the chemical reaction rate, especially at low Br$_2$ contents

in methanol. In this case InP, InAs and GaAs dissolving in the bromine-methanol solutions occurs according to mixed kinetics.

When InSb is treated with a bromine-methanol solution, then a stoichiometric In/Sb proportion retains in the surface layers [4]. Etching of InSb in the 0.5 vol.% Br$_2$ in CH$_3$OH solution leads to formation of a surface oxide film (up to 3 nm thick). This film is made up of a mixture of In$_2$O$_3$ and Sb$_2$O$_5$ [5]. Use of 5 vol.% Br$_2$ solution in methanol for InP treatment enables one to obtain surfaces with the lowest amount of impurities [6]. For local etching of indium phosphide a Br$_2$ solution in dimethylformamide is recommended [7].

As bromine dissolver, not only organic solvents but hydrobromic acid may be used. The latter exhibits high complexing ability and can dissolve in it (and hold for long) rather big amounts of Br$_2$, contrary to organic solvents (e.g., CH$_3$OH or C$_2$H$_5$OH) that intensively evaporate during the sample cutting, with bromine quickly volatilizing. Besides, methanol is very toxic, and viscous ethylene glycol (although being less toxic) is more suitable for polishing compositions at low Br$_2$ contents. For chemical etching and chemical cutting of CdTe, Br$_2$ in HBr solutions are used; dissolution processes occurring in this case have been adequately studied [8]. For chemical cutting of InSb the 20 vol.% Br$_2$ solution in HBr has been offered [9]; the authors, however, have not given any information on the kinetics of dissolving. Chemical dissolution of InAs in the Br$_2$-HBr solutions has not been studied up to setting the problem by us in this paper.

2. Results and discussion

The objective of this paper is to investigate processes of InAs chemical dissolution in the Br_2-HBr solutions, as well as to optimize both compositions and technological procedures used at InAs polishing and chemical cutting in the above solutions.

The InAs dissolution rate was found using a unit for chemico-dynamic polishing in which the hydrodynamic rotation of a disc has been realized. This enabled us to measure the etching rate keeping the thickness of the boundary diffusion layer constant. Our experiments were performed for single-crystal undoped n-InAs samples. The wafers whose areas were about 0.5 cm^2 have been cut from ingots and, after mechanical grinding and polishing, etched in a polishing solution to remove the layer that has been disrupted at cutting, grinding, and chemico-mechanical polishing. The substrates have been put into a special fluoroplastic holder. The dissolution rate was determined from the wafer thickness decrease using a IC-1 clockwork indicator. Three or four samples were being dissolved at a time.

Chemical cutting was made using an updated machine for chemical cutting SKhR-2. The essence of chemical cutting is that a thin layer of water solution of a reagent is put on the cutting string (wire) surface. This wire is sliding over the surface of the cut sample, being forced against it by a preset effort (about 10^{-2} N). The layer of the reagent water solution serves as a lubricant. At the areas where the solution is in contact with the cut sample surface (i.e., near the wire) the chemical dissolution of the sample material occurs. The products diffuse from the sample surface into a gap between it and the wire, and then are being carried out of the gap. As the surface is etched off the sample is also transferred towards the wire. The velocity of this transfer is equal to that of the surface dissolution (etching off), so the pressure exerted by the string on the sample during the chemical cutting process remains the same.

The chemical cutting rate was calculated from the time needed to cut two or three plates off the same InAs single crystal (that has the shape of a parallelepiped). The Br_2 concentration in solutions changed but slightly during etching and cutting (about 10-15 min). Chemical etching was performed at a temperature of 22°C, while chemical cutting was performed at 15°C, with the aim to stabilize the dissolution rate and prevent the Br_2 volatilization.

Shown in Fig.1 are the concentration dependencies of the etching and chemical cutting rates for indium arsenide. One can see that (as in the case of InAs dissolving in the bromine solution in methanol [3]) the dissolution rate grows linearly with bromine content at Br_2 concentrations up to 6-7 vol.%. At further increase of bromine concentration the dissolution rate slows down a little. But when the Br_2 concentration reaches 20 vol.%, then the indium arsenide dissolution rate begins to rise steeply. If the solutions are used that contain over 33 vol.% Br_2 in hydrobromic acid, then the interaction rate becomes too high to be accurately measured, due to disintegration of the surfaces of dissolving samples.
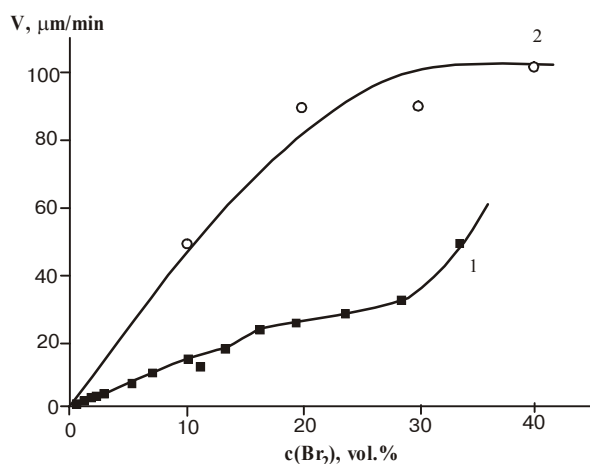

Fig.1. Concentration dependencies of the InAs chemical etching rate (1) and chemical cutting (2) in the Br_2-HBr solutions.

At low bromine concentrations the chemical cutting rate increases much more steeply than in the case of chemical etching. A possible explanation is that the active solution is supplied just to a narrow gap where the sample is cut, and the products of interaction are immediately carried out of the interaction area. Besides, one should not neglect a mechanical interaction between the string and sample that favors removal of the surface film made of the interaction products. Further increase of bromine concentration makes the chemical cutting rate to flatten out at 20-30 vol.% Br_2. Slowing down of the chemical cutting rate at high bromine concentrations may be explained by high volatility of bromine. This prevents to supply a solution with high Br_2 content to the place where cutting occurs. When such solutions are transported with a string, the bromine concentration goes down steeply with time. So the optimum solution to be used for chemical cutting is that where the Br_2 content is 20 vol.%.

As in the case of CdTe chemical etching with Br_2 solutions in hydrobromic acid [8], at low bromine concentrations the rate of In etching in such solutions should be determined by the rate of bromine diffusion to the surface of dissolved sample. It is low-concentration solutions of bromine that are used to chemically polish semiconductor compounds. To find out in what (diffusion or kinetic) region the InAs dissolution in the low-concentration Br_2-HBr solutions occur, we have plotted the dissolution rate (v) versus disc rotation rate (r) curves in the v^{-1}-$r^{-1/2}$ coordinates [3,10]. If the process is limited with diffusion, such curves pass through the origin of the coordinates. An increase in importance of chemical reaction during the total dissolution process results in a decrease of the angle of inclination of the above curves and, in the limit (when the chemical interaction rate is the rate-determining factor for the total dissolution process) the straight lines become parallel to the x-axis.

From Fig. 2 one can see that the process of InAs dissolution in 1 and 2 vol.% Br_2 solutions in HBr is determined by a mixed kinetics because the straight lines are non-parallel to the x-axis and there are y-intercepts.

Shown in Fig. 3 are the InAs dissolution rate versus temperature curves for those above solutions where the effect of angular motion rate on the dissolution rate was studied. From these curves we have calculated the apparent activation energy values (E_a). It is commonly supposed [10] that those processes in water solutions for which $E_a < 35\text{-}40$ kJ/mole are controled by the diffusion rate; at $E_a > 40$ kJ/mole the process rate is immediately determined by the chemical reaction rate. Our results indicate that the dissolution process is controled with diffusion, since the apparent activation energy for InAs dissolution in 1(2) vol.% Br_2 solution in HBr is 11.2 (18.0) kJ/mole. Some nonconsistency between the results obtained when studying how the InAs dissolution rate depends on the disc rotation rate (mixed kinetics) and temperature (diffusion limitation of the process) may be attributed either to the fact that in the case of mixed kinetics the diffusion processes dominate, or to the fact that the activation energy of chemical interaction is too low.
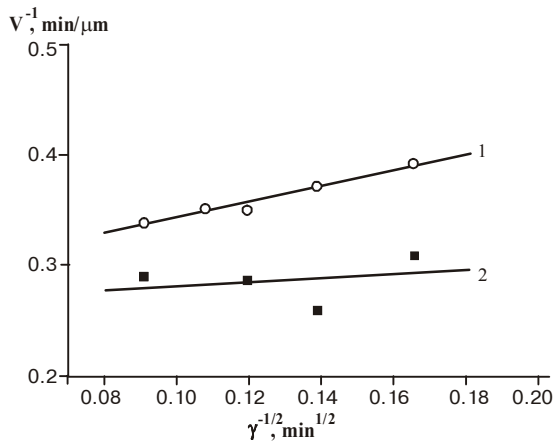

Fig.2. Dependence of the rate of InAs dissolution in the 1(1) and 2 vol.% (2) Br_2 solutions in HBr on the stirring rate.
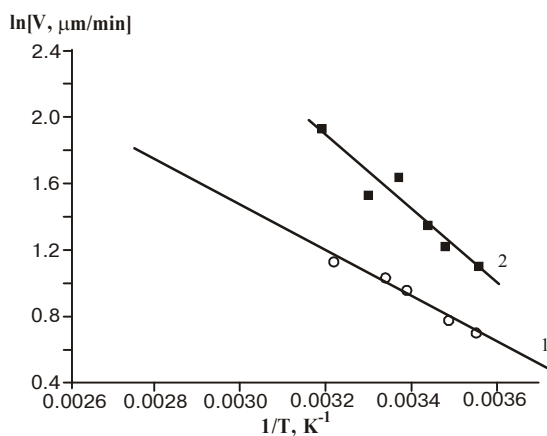

Fig.3. Temperature dependence of the rate of InAs dissolution in 1 (1) and 2 vol.% (2) Br_2 solutions in HBr.

Conclusions

It was found that the rate of InAs dissolution in the Br_2 solutions in HBr grows linearly with bromine concentration at low (up to 6 vol.%) Br_2 content. Such solutions may be used to chemically polish InAs. The best surfaces are obtained, at 2.0-5.0 vol. % Br_2 content in the solution; the etching rate varies from 5 to 10 μm/min at 22°C and disc rotation rate $r = 52$ min^{-1}. The solutions that contain 20-30 vol.% Br_2 in HBr dissolve InAs with the rate of 25-50 μm/min, forming polished surfaces with etch pits. The results obtained enabled us to optimize both solution compositions and technological conditions used for InAs cutting. These are 20 vol.% Br_2 in HBr at 15°C and the tungsten string (80 μm in diameter) velocity of 25 cm/s.

References

1. V.V. Starovoitova, V.A.Sannikov, Study of the process of indium antimonide etching in the dimethylformamide glycerin-bromine system (in Russian) // Elektronnaya Tekhnika, Ser. 6. Materialy No.11, pp.106-109 (1980).
2. S.V.Temerev, Kinetics of indium antimonide and indium arsenide chemical dissolution in the bromine-methanol-carbon tetrafluoride system (in Russian) // Zhurn. Fiz. Khim. **63**(8), pp.2226-2228 (1989).
3. V.A.Perevoschikov, Processes of chemicodynamic polishing of semiconductor surface (in Russian) // Vysokochistye Veschestva No.2, pp.5-29 (1995).
4. J.D.Contor, M.Dupuy, M.Royer, Effect l'erosion chimique et ionique sur des monocristaux (111) d'antimoniure d'indium: analyse par microscopie electronique et par spectroscopie de photo-electrons // J.Microsc. et Spectrosc. Electron. **5**(2), pp.201-206 (1980).
5. X.Tang, R.G.Van Welzenis, F.M.Van Setten, A.J.Bosh, Oxidation of the InSb surface at room temperature // Semicond. Sci. and Technol. **1**(6), pp.355-365 (1986).
6. P.G.Dvoryankina, V.F.Dvoryankin, N.Ya.Cherevatskii, Effect of chemical treatment and ion bombardment on the InP {100} surface composition (in Russian) // Poverkhnost'. Fizika, Khimiya, Mekhanika No.8, pp.108-113 (1989).
7. L.I.Vozmilova, M.M.Berdichenko, Investigation of GaAs and InP local etching with bromine dimethylformamide solution (in Russian) // Izv. AN SSSR. Neorgan. Mater. 16(1), pp.13-17 (1980).
8. A.A.Sava, V.N.Tomashik, A.V.Fomin, M.Yu.Kravetski, O.A.Yakubtsov, V.K.Puzhevich, V.I.Makhnyuk, Chemical dissolution of cadmium telluride in the Br_2-HBr system solutions (in Russian) // Izv. AN SSSR. Neorgan. Mater. **25**(12), pp.1997-2001 (1989).
9. N.N.Grigor'ev, M.Yu.Kravetski, A.V.Fomin, An approximate model for process of chemical cutting of thin crystalline wafers (in Russian) // Optich. Zhurn. N 8, pp.71-72 (1993).
10. B.D.Luft, V.A.Perevoschikov, L.N.Vozmilova et al., Physico-chemical Techniques for Semiconductor Surface Treatment (in Russian), Radio i Svyaz', Moscow, 1982.