Gibbs Diagrams in the Chemical Etching of Semiconductors

Z.F. Tomashik, Ye.O. Bilevych, V.M. Tomashik, N.V. Kusiak and O.R. Gumeniuk
Institute for Semiconductor Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine

Abstract
The velocity of semiconductor dissolution is a quantitative characteristic of the etching process and one of the main etchant properties. Therefore, it is necessary to investigate the concentration dependence of semiconductor dissolution for all etchant compositions. It is shown that such dependencies for three component etchants can be represented as surfaces of equal etching rate or Gibbs diagrams. The diagrams "etching rate of semiconductor (mμ/min) – etchant composition" of the different systems, using nitric acid, hydrogen dioxide, iodine and potassium bichromate as oxidizing agent were constructed by mathematically planning the experiment. Such diagrams provide the opportunity to compare different etchant compositions by their etching rates and other properties and selection of the best etchant for a given semiconductor compound.
Keywords: Gibbs diagram, chemical etching, etchant composition, etching rate.

The development of modern semiconductor materials science and semiconductor device manufacture is closely related to the advance in processing and preparation of semiconductor surfaces. The obtaining of high quality surfaces of semiconductor materials, which have perfect structure and geometry and homogeneous chemical composition, has exceptional importance in the manufacture of semiconductor devices. Now these problems are successfully resolved by chemical wet etching [1982Luf, 1995Per]. The velocity of the semiconductor dissolution is the quantitative characteristic of the etching process and one of the main etchant properties. Therefore, it is necessary to investigate the concentration dependence of semiconductor dissolution for all etchant compositions. Such dependencies for three component etchants can be represented as surfaces of equal etching rate or Gibbs diagrams.

The diagrams "etching rate of semiconductor (mμ/min) – etchant composition" of the different systems, using nitric acid, hydrogen dioxide, iodine and potassium bichromate as oxidizing agent were constructed mathematically planning the experiment. Such diagrams provide the possibility to compare the different etchant compositions by their etching rates and selection of the best etchant for a given semiconductor compound.

The dependence of the etching rates of semiconductors on etchant compositions of different etching systems have been studied in reproducible hydrodynamic conditions using a rotating disk. The experiments were performed using single-crystal wafers with a surface area of about 0.5 cm^2 and thickness of 1.5-2 mm, which were cut from ingots. Prior to the etching, the wafers were mechanically polished, and the surface layer of 50 to 80 μm in depth was removed with the etchant of the same composition as that used subsequently for studies of the etching process. Etchants were made just prior to use from high purity starting materials. The samples were attached to quartz substrates using pizzeine and then mounted in a holder allowing measurements to be taken during rotation of the samples (with a rotation rate ranging from 36 to 120 min^{-1}). After processing, the samples were washed with distilled water.

The etching rate was determined by the reduction in wafer thickness using an ICh-1 time indicator (accuracy of measurement was 0.5μm). Two or three samples were etched simultaneously, with a difference in the measured thickness not exceeding 5 %. Before etching, all etchants were allowed to stand for 40-80 min in order for the chemical reactions taking place between the etchant components to achieve equilibrium conditions. The solutions were prepared using 70 % HNO_3, 30 % H_2O_2, 13 % $K_2Cr_2O_7$, 34 % HCl, 40 % HBr, 55 % HJ, 100 % acetic, 27 % tartaric, 20 % citric, 9 % oxalic and 40 % lactic acids.

Using the Gibbs diagram, we are also able to study the dopant influence on the etching rate. For example, the surfaces of equal etching rate for undoped and tin doped InAs are shown in the Fig. 1. Comparing these two Gibbs diagrams, one can see that the doping of semiconductors can strongly influence the etching rate. In the case of tin doped InAs, the doping leads to a decrease in the etching rate. This can be explained by the

retardation of the InAs dissolution velocity in the presence of tin compounds that can be formed during the chemical etching of such material.
The Gibbs diagrams also provide the possibility to determine a mechanism for the interaction of the semiconductor with the etchant during chemical etching. We can conclude that the dissolution of cadmium telluride in the solutions HNO_3-HCl-CH_3COOH is limited by the interaction of tellurium, which is formed on the surface, with the etchant components, if we compare the surfaces of equal etching rates (Gibbs diagrams) of CdTe and Te in such solutions (Fig. 2).
Using the surfaces of equal etching rates (Gibbs diagrams) for the interaction of solid solutions with a given etchant it is also possible to determine the influence of solid solution composition on the mechanism of its dissolution.
However, for the chemical treatment of semiconductor surfaces it is necessary to know not only the etching rate but also the surface roughness (R_Z), degree of surface contamination with the etchant components and reaction products, and some other characteristics. Therefore, the concentration dependencies of all these parameters also must be constructed in the form of Gibbs diagrams. One can chose the best etchant for a given semiconductor if a selection of such diagrams are constructed and compared with each other. The plotting of Gibbs diagrams for the chemical etching of semiconductor compounds is the scientific basis for the preparation of the best etchant composition for a given technological process.
Using the Gibbs diagrams, the three-component etchants with differing etching velocities, surface roughness (R_Z), degree of surface contamination with etchant components and interaction products and some other characteristics have been determined for the chemical treatment of InAs, InSb, GaAs, CdTe and $Cd_{1-x}Hg_xTe$ and $Zn_xCd_{1-x}Te$ solid solutions. The liquid solutions of the HNO_3-HCl (HBr, HJ)-organic acid, H_2O_2-HBr-organic acid and $K_2Cr_2O_7$-HBr-HCl (organic acid) systems were used for the formulation of the different etchant compositions (we used oxalic, acetic, lactic, tartaric and citric acids as the organic acids) [1999Tom, 2001Bil, 2001Tom1, 2001Tom2].

References

[1982Luf] Luft, B.D., Perevoshchikov, V.A., Vozmilova, L.N., et al., "Physico-Chemical Methods of Semiconductor Surface Processing" (in Russian), Moscow, "Radio i sviaz'", 1-136 (1982) (Review, Chem. Treatment)

[1995Per] Perevoshchikov, V.A., "The Chemicodynamic Polishing of Semiconductor Surfaces" (in Russian), *Vysokochistyie veshchestva*, (2), 5-29 (1995) (Review, Chem. Treatment)

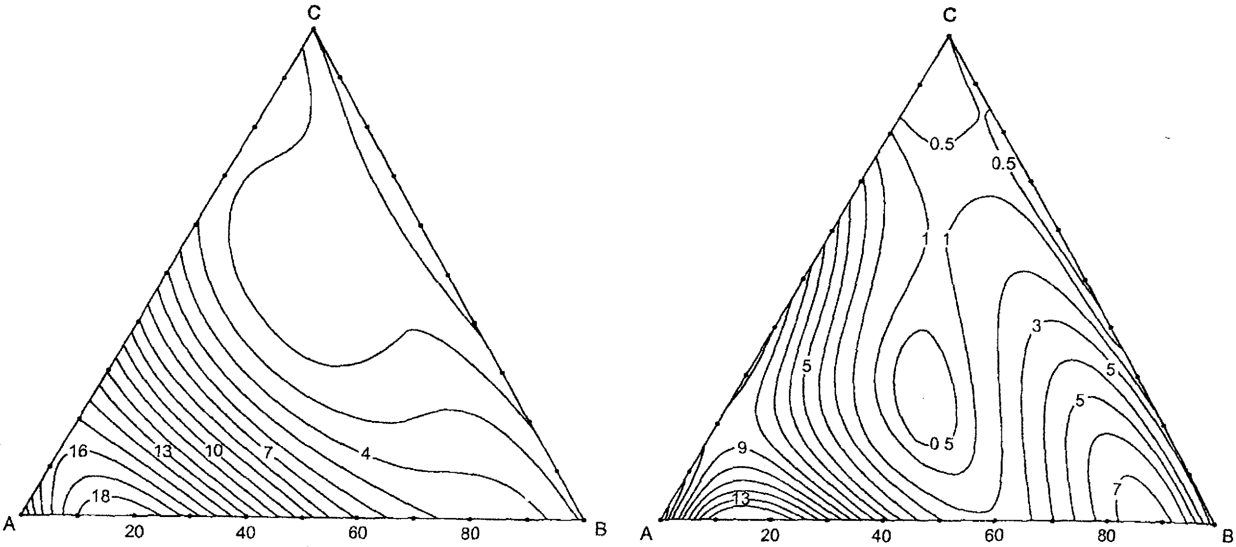
[1999Tom] Tomashik, Z.F., Danylenko, S.G., Tomashik, V.N., "Dissolution of Indium Arsenide in the HNO_3-HBr-H_2O Solutions", *Proceeding of SPIE*, **3890,** 478-485 (1999) (Experimental, Chem. Etching)

[2001Bil] Bilevych, E.O., Tomashik, V.N., Tomashik, Z.F., Danylenko, S.G., "Chemical Etching of $Cd_xHg_{1-x}Te$ Solid Solution Single Crystals in Solutions of HNO_3-HCl-Organic Acid Systems", *Functional materials*, **8**(3). 488-492 (2001) (Experimental, Chem. Etching)

[2001Tom1] Tomashik, V.N., Tomashik, Z.F., Danylenko, S.G., Bilevich, Ye.O., "Chemical Dissolution of III-V and II-VI Semiconductor Compounds in the Solutions of HNO_3 – HCl – Lactic Acid System", *Proceeding of SPIE.* **4355,** 252-257 (2001) (Experimental, Chem. Etching)

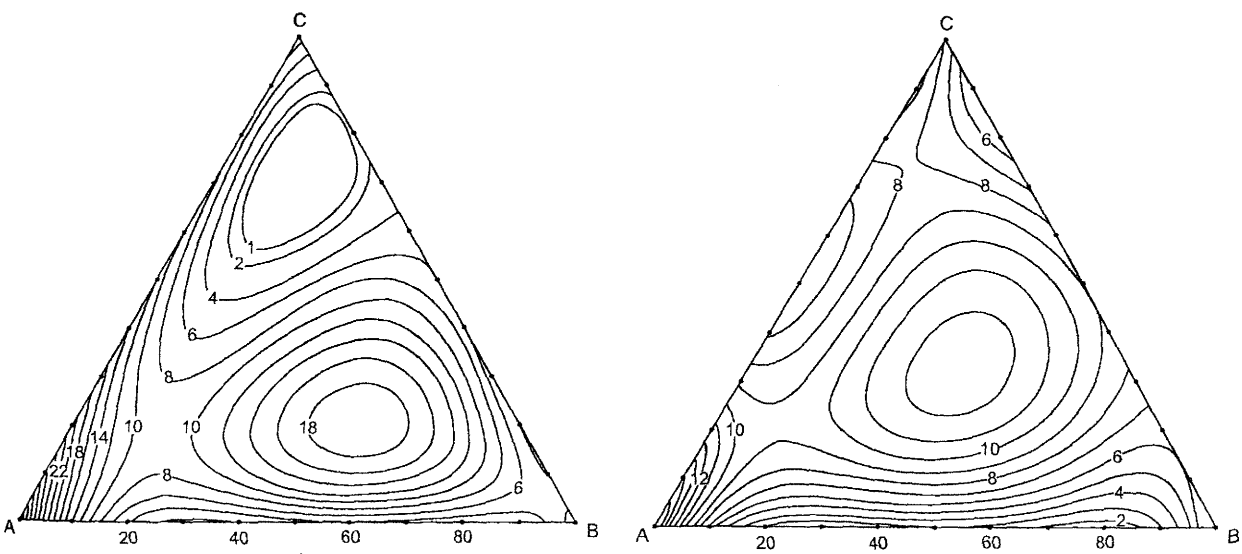
[2001Tom2] Tomashik Z.F., Bilevych Ye.O., Tomashik V.N., "Interaction of Cadmium Telluride with the Solutions of the HNO_3-HCl(HBr)-Tartaric Acid" (in Russian), *Kondens. Sredy i Mezhfaz. Granitsy*, **3**(3) 237-241 (2001) (Experimental, Chem. Etching)

ISBN 3-932120-45-0



a) b)

Fig. 1: The Gibbs diagrams (the surfaces of equal etching rates, µm/min) of undoped (a) and Sn doped InAs (b) in H_2O_2-HBr-lactic acid solutions [the ratio of H_2O_2 : HBr : lactic acid in A, B and C tops is (in vol %): A – 10 : 90 : 0; B – 20 : 20 : 60; C – 50 : 50 : 0]



a) b)

Fig. 2: The Gibbs diagrams (surfaces of equal etching rates, µm/min) of CdTe (a) and Te (b) in the HNO_3-HCl-CH_3COOH solutions [the ratio of HNO_3 : HCl : CH_3COOH in the A, B and C tops is (in vol %): A – 10 : 90 : 0; B – 20 : 20 : 60; C – 90 : 10 : 0]

ISBN 3-932120-45-0