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Crystal Perfection of Si-rich SiGe Alloys Bulk Single –Crystals

Khutsishvili E., Gabrichidze L., Kobulashvili N.
Ferdinand Tavadze Institute of Metallurgy and Materials Science, Ministry of Education and Science,
Kazbegi 15, Tbilisi, 0160, Georgia, e-mail: elzakhutsishvili@yahoo.com

Abstract:
Crystal perfection of undoped and impurity-doped Si-rich SiGe alloys bulk single-crystals has been investigated. Influence of Ge atoms and doping by As and B on the crystal perfection of SiGe alloys in the composition range 0-2 at % Ge on the (111) plane are reported.
Keywords: *crystal perfection, single-crystals, SiGe alloys.*

1.Introduction

The SiGe alloys are one of the most advanced materials of the present century for high-frequency, analog, digital and other microelectronic and photonic devices. For these applications SiGe alloys are generally obtained as thin films grown on crystalline substrates. There observed strains and dislocations in these structures, which are major barriers to the investigation of intrinsic properties of SiGe alloys and their applications. To reveal the intrinsic properties of SiGe alloys it is necessary to study properties of their single crystals in bulk form.

For numerous applications of SiGe alloys the most important property in comparison with other basic factors is the structural perfection of their single crystals. Real single-crystals of SiGe alloys contain definite quantity of structural defects which considerably change their properties. More or less strict requirements for the crystal perfection of SiGe alloys require intense investigations in this direction.

In literature there have been studied SiGe alloys with large content of their constituent components [1-8]. There are very few literature data about structural peculiarities of undoped and heavily impurity-doped dilute SiGe alloys [9,10]. At the same time investigation of SiGe alloys namely for compositions near Si has attracted keen interest. It is known that small adding of isovalent impurity in basic material (as Ge in Si and on the contrary) significantly may improve the quality of main component [11].

In the present work investigations of crystal perfection of undoped and doped dilute single-crystals in the Si-rich side of SiGe alloys are presented.

2.Experimental Procedure

Undoped and impurity- doped single crystals of SiGe alloys in the composition range 0-2 at% Ge were grown by the Czochralski method from 48 mm diameter quartz cruicible with a large volume (exceeding several times the volume of final ingot, in order to minimize composition gradient of the melt) [10]. Si single crystalline rods of 50 mm length with [111] crystallographic orientations were used as seeds. During the process of pulling the crystal and the cruicible with the mother melt were revolved with the rate of 45 and 10 numbers of revolutions per minute in opposite directions The velocity for single-crystals growth was 0,25 mm per minute. Such conditions promote achieving of homogeneous distribution of alloy components and symmetry of temperature field on the crystallization front. The fusion was carried out in the helium atmosphere at a pressure of 50 kPa. First the melting camera was pumped off up to 10^{-4} mm Hg, then washed by flow of helium. At the end during the experiment the gas pressure remained constant (50 kPa). High purity crystals of n- Si ($n \approx 10^{11}$ cm^{-3}) and p-Ge ($p \approx 10^{13} cm^{-3}$) were charged into crucible. The product of chemical reaction SiO was removed from melting camera with equipped special apparatus for gas removing.

The composition of SiGe alloys and the uniformity of experimental samples were determined by X-raying. Dislocation structure has been studied by the method of chemical etching. Since dislocations density is lower than 10^6 etch pits per cm^2 we have observed dislocations on the microscope MIM-7 and Neophont. The samples of SiGe alloys single crystals with [111] orientation first were mechanically grinded, chemically polished in the mixture of HF:$HN0_3$(1:1), washed in the distilled water and etched for 30 minutes in the etchant $3HN0_3$:1HF:$8CH_3$ C00H for [111] orientation, 18 HNO_3:25HF :$5CH_3COOH$:0.1 Br_2: $10H_20$:!$Cu(NO_3)_2$ for [100]and[110] orientation. The current carriers concentration have been investigated at room temperature from Hall measurements by a common compensation method applying dc voltage. *p*-type impurity-doped SiGe alloys were doped by B, *n*-type impurity-doped SiGe alloys were doped by As . Characteristics of experimental samples of SiGe alloys are listed in the Tables 1-3.

3. Results and discussion

Undoped Si-Ge alloy. Undoped samples of SiGe alloys were *p*-type. The investigation of crystal perfection of SiGe alloys samples with different plane orientations (110), (111), (110) has shown, that the least dislocation density is observed for (111) plane (Table 1).

TABLE 1. Characteristics of undoped SiGe alloys single crystals at room temperature.

№ of samples	Content of Ge, at%	Carriers concentration,cm^{-3}	Plane orientation	Dislocation density,cm^{-2}
1	0.6	$3.3 \cdot 10^{14}$	(111)	$6.9 \cdot 10^4$
2	0.9	$1.3 \cdot 10^{17}$	(111)	$2.6 \cdot 10^5$
3	2.0	$9.0 \cdot 10^{15}$	(110)	$1.3 \cdot 10^5$
4	2.0	$9.0 \cdot 0^{15}$	(111)	$8.5 \cdot 10^4$
5	2.0	$9.0 \cdot 10^{15}$	(110)	$1.3 \cdot 10^5$
6	2.0	$9.3 \cdot 10^{15}$	(100)	$1.5 \cdot 10^5$
7	2.2	$9.7 \cdot 10^{16}$	(111)	$9.2 \cdot 10^4$

At that studies on the fixed (111) plane showed, that dislocation density increases with Ge content increasing. However homogeneous distribution of dislocation etches observed in Si is not broken in SiGe alloys up to 0.4 at% Ge composition in Si(Fig.1).

Fig.1.Dislocation structure of SiGe alloy single crystal with 0.4at%Ge(x1000) on the plane[111]

In single crystals of SiGe alloys with content of Ge bigger than 0.4 at% the dislocation density not only increases with increasing of Ge composition, but there observed separate accumulation of dislocation etches and consequently disturbance of their homogeneous distribution in experimental samples (Fig .2).

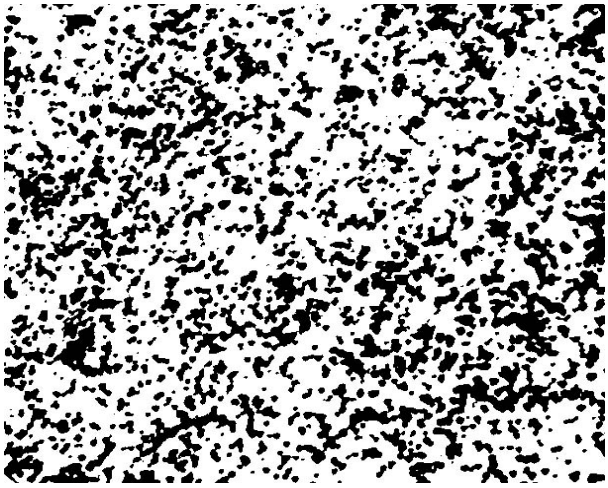

Fig.2..Dislocation structure of SiGe alloy single crystal with 1.4at%Ge(x1000) on the plane[111].

In this way the investigation of crystal perfection of undoped Si and dilute SiGe alloys on the (111) plane shows that increasing of Ge content in Si rises the dislocation density and disturbs their homogeneous distribution. Disturbance of dislocation density rises with increasing of Ge concentration. Impurity doping of Si and dilute SiGe alloys changes the structure of undoped samples. But this changes is not the same in the *n*- and *p*- types samples.

***p*-type impurity-doped SiGe alloy.** Metallographic investigations of B doped dilute SiGe alloys have shown, that appropriateness of density of dislocations etches dependence versus Ge composition, observed for undoped SiGe alloys, does not change too much: density of dislocations etches increases with increasing of Ge content. But values of density of dislocations etches in B doped Si and dilute SiGe alloys are noticeably increased in comparison with those for undoped alloys. Increasing of B doping degree increases density of dislocations etches. But boron atoms introduce less disturbance, than Ge atoms. Analysis of data for slightly doped samples of SiGe alloys(p~10^{16}cm^{-3}) shows that at increasing of Ge content in 2 times density of dislocations increases ~8 times (samples 1 and 3,Table2). At that the increase of B concentration by 3 orders increases density of dislocations etches in 3 times(samples 1 and 2,Table 2). There observed also noticeable disturbance of homogeneity of dislocations distribution on surface of the plane for samples heavily doped by B.

TABLE 2. Characteristics of doped by B SiGe alloys single crystals at room temperature.

№ of samples	Content of Ge, at%	Carriers concentration,cm^{-3}	Plane orientation	Dislocation density,cm^{-2}
1	1.0	$3.2\cdot10^{16}$	(111)	$1.2\cdot10^{4}$
2	1.0	$4.0\cdot10^{19}$	(111)	$4.0\cdot10^{4}$
3	2.0	$7.0\cdot10^{16}$	(111)	$9.0\cdot10^{4}$

***n*-type impurity-doped SiGe alloys.** Studies has shown, that adding of Ge in Si up to 2.0at% in slightly doped by As(n~10^{16} cm^{-3}) SiGe alloys causes the increase of amount of dislocation etches

(Table 3).The dislocation density of experimental samples of poorly doped by As(~10^{16}cm^{-3}) SiGe alloys is 1.7 10^4 etch pits per cm^2 at 1 at%Ge and 1.1 10^5 etch pits per cm^2 at 2 at%Ge.

TABLE 3. Characteristics of doped by As SiGe alloys single crystals at room temperature

№ of samples	Ge content ,at%	Carriers concentration,cm^{-3}	Plane orientation	Dislocation density,cm^{-2}
1	1.0	10^{16}	(111)	$1.7\cdot10^4$
2	2.0	10^{16}	(111)	$1.1\cdot10^5$

But heavily As impurity doping (n~10^{19} cm^{-3}) of Si and dilute SiGe alloys significantly changes the structure of undoped samples. If there were found out dislocations in samples along the full length of ingot of heavily doped by B, *n*-type samples unlike p-type samples behaved differently. There is not revealed dislocation structure at heavily doping by As. It is in accord with the data for impurity-doped *n*-Si[12]. So dilute heavily impurity-doped SiGe alloys by As are similar impurity-doped n-Si. The rise of impurity concentration in a sample is not always additional source of dislocations. The reverse may be true. At certain concentration of doping impurity dislocations disappeared in *n*-Si. At doping of Si by P and As crystals became dislocation-free since impurity concentration of $5\cdot10^{17}$cm^{-3}. In [12] it has been shown, that in such single crystals the most part of dislocations heritable from seed gradually grows to surface. This leads to decrease of density of dislocations and at last to disappearance of dislocations. The increase of doping impurity in the crystal hastens process of dislocations disappearance .One of the decisive factors determinant crawl of dislocations to surface is the increase of vacancies concentration. At introduction of enough amount of donor impurity equilibrium vacancies concentration may greatly grow. Noticeable influence of donor impurities on the vacancies concentration and accordingly on the crawl of dislocations in the process of crystal growing will reveal starting with impurity concentration of $5\cdot10^{17}$cm^{-3}. It is confirmed by reverse influence of acceptor impurity. At introduction of acceptor impurity equilibrium vacancies concentration decreases. It let us to suppose, that observed phenomenon in SiGe alloys may be connected with vacancy mechanism of dislocations going out to the crystal surface. In dilute SiGe alloys heavily impurity-doped by As there revealed cell type structure like Si single crystals doped by As.

4.Summary

Investigation of crystal perfection of undoped SiGe alloys bulk single-crystals with content of Ge in the range of 0-2 at % have shown, that increasing of Ge content in Si rises the dislocation density and disturbs their homogeneous distribution. At that disturbance of dislocation density rises with increasing of Ge concentration The influence of impurity doping of Si and dilute SiGe alloys on the structure of undoped samples is not the same in *n*- and *p*- types of samples.

In dilute SiGe alloys impurity-doped by B the dependence of dislocation etches distribution on Ge concentration is similar the dislocation structure of undoped dilute single crystals of SiGe alloys. But values of density of dislocations etches in B doped Si and dilute SiGe alloys are noticeably increased in comparison with those for undoped alloys. But dislocation structure is not revealed in heavily doped *n*-type samples of SiGe crystals. So dilute heavily impurity-doped SiGe alloys by As are similar impurity-doped n-Si.

Comparison of structure perfection of SiGe alloys single crystals samples with different orientations of surfaces (110) (111) (110) has shown, that the least dislocation density is observed for the (111).

REFERENCES

1. Кекуа М.Г., Хуцишвили Э.В., Твёрдые растворы полупроводниковой системы германий-кремний, Тбилиси, Мецниереба, 1985.
2. Yonenaga, I., Growth and Fundamental Properties of SiGe Bulk Crystals, J. Cryst. Growth, 2005, vol. 275,pp. 91–98.
3. Yonenaga, I. and Nonaka, M., Czochralski Growth of Bulk Crystals of Ge1 – *x*Si*x* Alloys: II. Si-Rich Alloys, J.Cryst. Growth, 1998, vol. 191, pp. 393–398.
4. Yonenaga, I. and Murakami, Y., Segregation during the Seeding Process in the Czochralski Growth of GeSi Alloys, J. Cryst. Growth, 1998, vol. 191, pp. 399–404.
5. Yang, D., Yu, X., Ma, X., et al., Germanium Effect on Void Defects in Czochralski Silicon, J. Cryst. Growth, 2002, vol. 243, pp. 370–371.
6. Volz, M.P., Motakef, S., and Szofran, F.R., Bridgman, Growth of Detached GeSi Crystals, J. Cryst. Growth, 2002, vols. 237–239, pp. 1844–1848.
7. Deitch, R.H., Jones, S.H., and Digges, T.G., Bulk Single Crystal Growth in Silicon–Germanium, J. Electron. Mater., 2000, vol. 29, no. 9, pp. 4–5.
8. Sheng, S.R., Dion, M., McAlister, S.P., and Rowell, N.L.,Growth and Characterization of Ultrahigh Vacuum/Chemical Vapor Deposition SiGe Epitaxial Layers on Bulk Single-Crystal SiGe and Si Substrate, J. Vac Sci. Technol., 2002, vol. 20, pp. 1120–1124.
9. Кекуа М.Г., Белокурова И.Н., Труды Института Металлургии АН ГССР, Вопросы металловедения и коррозии металлов. Исследование совершенства структуры монокристаллов германия ,легированного кремнием. Тбилиси, Мецниереба,1971, pp.18-22. .
10. Kekua, M.G., Darsavelidze, G.Sh., and Pagava, M.O., Radial Homogeneity of an $Si_{0.98}Ge_{0.02}$ Crystal, Inorg. Mater., 1999, vol. 35, no. 1, pp. 4–6
11. Дж.Гарстон, Р.Хоникомб. Дислокации и механические свойства кристаллов. Москва, Иностранная литература,1960.
12. Фистуль В.И.,Сильнолегированные полупроводники, Москва, Иностранная литература,1967.

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