Influence of High Temperature Annealing on Electrophysical Characteristics and Internal Friction of Iron Doped Boron

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ABSTRACT: After high temperature annealing iron doped boron with hole concentration > 10^{17} sm"^{3} has changed its conductivity from p- to n-type, with the ten times increase of electron carrier concentration and of electron mobility from 5 to 20 sn^V'sec"^{1}. Simultaneously micro-hardness and shear modulus have increased by 10-15%. Internal friction measurements of annealed samples showed that the main peak at 250°C attributed to twin boundary migration separated and formed two peaks, he observed changes may be explained by the annealing of planar defects and shifting of iron atoms, previously segregated on defects to electrically more active positions in solid solution. The splitting of internal friction maximum can be connected to moving twin boundaries interacting with different types of solute complexes.

1. INTRODUCTION

Boron and its alloys with transition metals are promising materials for modern semiconductor devices employed in extreme conditions like prolonged heating, irradiation and high stresses. This type of exploitation is accompanied with radical changes in the distribution and concentration of impurities and structural imperfection, which may induce degradation of various physical parameters of boron based alloys. From this point of view it is interesting to investigate the influence of prolonged high temperature annealing on electrophysical characteristics and structure-sensitive physico-mechanical properties of crystalline boron alloyed with transition metals.

According to published data (Golikova, 1979, Werheit et al., 1981) definition of the type of conductivity of boron alloyed with transition metals is the problem that remains unclear. At low concentrations of alloying elements (<2 at.%) boron conductivity is conditioned by hole carriers, while at higher concentrations conductivity changes to n-type (Gabunia et al.,1974, Arifov et al.1974, Kuhlman et al., 1990).

2. EXPERIMENTAL

Investigations were earned out on massive crystals of ß-rhombohedral boron alloyed with Fe up to 2%. The concentration and mobility of charge carriers of alloyed boron samples were determined together with room temperature microhardness and temperature dependence of internal friction (IF) and thermal expansion coefficient (TEC) in initial condition and after annealing in 10"^{5} mm mercury col. vacuum at 1000°C during 100 hr.

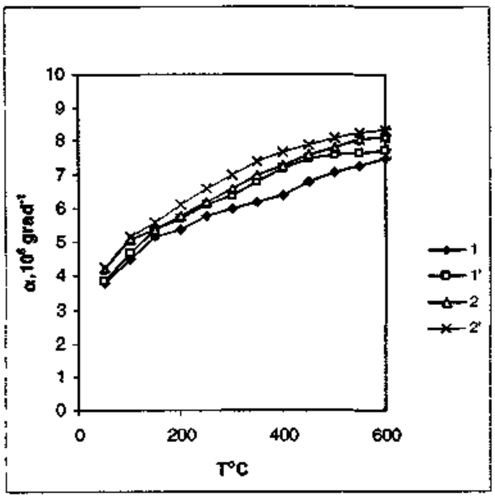
Bulk crystals of doped boron were prepared by melting of appropriate charge placed in boron nitride crucibles in resistance furnace with tungsten heater. The melting was conducted in inert atmosphere and volatilization of charge was less than 0.5 - 0.8 mass %. In many cases only upper part of the charge was melted and lower part remained hollow. Inside this hollow part columnar and planar crystals with regular facets and their accretions were formed. Typical dimensions of the crystals were 1 mm^2 in cross-section and 5-10 mm in length.

Charge carriers concentration, their mobility, microhardness and temperature dependence of TEC and IF were measured. Physical-mechanical characteristics of iron doped boron are given in Table 1.

Concentration and mobility of charge carriers were determined by Hall coefficient measurements in constant magnetic field with 10^4 Ersted tension. For unalloyed samples p-type and 1.10^{17} sm~^{3} charge carrier density were characteristic. After annealing at 1000°C in 10"^{5} mm. mere, vacuum during 100 hr the type inversion of conductivity and increase of electron concentration up to 2.10^{18} sm"^{3} were observed. The mobility of electrons also increased significantly in comparison with boron alloyed with nickel (Darsavelidze et al 2002). Unfortunately, no comparison with electrophysical characteristics of similarly prepared unalloyed boron was possible as their electroresistance was very high.

Microhardness of alloyed samples at room temperature was measured on PMT-3 type instrument with 3% accuracy (see Table 1). After annealing hardness of alloyed specimens increased more than in unalloyed boron, where the increase was insignificant- from 3000 to 3200 kg/mm^2.

The thermal expansion coefficient was determined on a dilatometer with induction transducer in 10"^{3} mm mere, vacuum. The accuracy of measurements for specimens with the dimensions 4x4x12 mm^3 was ±3% for relative elongation and ±5% for TEC. A well defined inflection at 200-450°C was observed on the TEC-temperature curve (fig.l). Above 500°C TEC increases almost linearly with temperature. TEC values are approximately 10% higher then those given in (Tsagareishvili et. al., 1990). At cooling, hysteretic loop of TEC is observed in the 500-200°C temperature interval which is invariably repeated at thermal cycling. After anneaUng at 1000 C a small increase of TEC values in the whole temperature interval and significant decrease of hysteresis was established. Thermal cycling induced no changes in TEC-temperature curves.



Figurel. Temperature dependence of thermal expansion coefficient in iron doped boron (1.5at%). Annealing (1) and cooling (1') of Initial specimen,' Annealing (2) and cooling (2') of annealed specimen.

On low frequency (~ 5 Hz) internal friction curves of unalloyed boron three peaks were found at 250, 300 and 450°C. It was established earlier (Tsagareishvili et.al., 1972) that peak at 300°C is not connected with relaxation processes and those at 230-250°C and 400-450°C are relaxation peaks (Darsavelidze et. al., 1986). Estimations by Marx-Wert method revealed (Postnikov, 1974) that high maximum at 250°C is characterized by 1.3 eV activation energy and 5.10^{12} sec"^{1} frequency factor, while for peak at 450°C values 2.2 eV and 8.10^{14} sec"^{1} are typical (table 1).

Unalloyed as well as alloyed boron is characterized by rather complicated temperature dependence of relative dynamic shear modulus. The most significant decrease of modulus is observed at the highest peak temperature, although for other peaks small modulus defects are also typical.

The amplitude dependence of modulus defect and of internal friction at 250°C is such that these quantities are increasing with the increase of amplitude, while for other maximums these characteristics are independent from deformation amplitude up to 1-10"^{3}.

Table 1. Physical-mechanical characteristics of Fe-doped boron.

Specimen State	Conductance Type	Carrier concentration, cm"^{3}	Mobility, crn^-V^1	IF Maximum Temperature, °C	Nature of maximum	Activation Energy, eV	Frequency Factor, e"^{1}	Microhardness, kg/mm^2	Shear Modulus, GPa
Initial	p	MO^{17}	15	530 570 430	Relax. Non-relax. Relax..	1.3 2.2	5 10^{12} 8 10^{14}	3300	170
Annealed at 1000°C ,100h	n	2-10^{18}	25	460 530 570 400	Relax. Relax. Non-relax. Relax.	0,8 1,3 1,8	MO^{12} 5-10^{12} M0^{14}	3800	210

Observed changes after annealing of iron doped boron samples may be conditioned by characteristic structural defects - twins and packing faults in {100} planes (McKelvey et.al., 1982), and by technological impurities interacting with them. At high temperatures part of structural defects may be annealed with the release of iron atoms segregated on them. In their regular positions of solid solution iron atoms are electrically more active and can create additional levels of electron donors (Nakayama et. al., 1997). At the same time the concentration of vacancies (electron acceptors) are lowered after annealing and so inversion of the type of conductivity pnd the increase of electron concentration in conductance zone may occur (see table 1).

These changes in electron structure caused by iron atoms as well as by other transition metals are accompanied by the formation of tight sp^1 type bonds (Lundström, 1983) and, as a result, by the increase of lattice parameter, hardness and shear modulus and decrease of TEC (see table 1).

The movement of twin and {100} packing fault boundaries are considered as the most probable mechanisms of processes inducing internal friction peaks at 250 and 400-450°C in boron (Tsagareishvili et.al., 1972, Darsavelidze et. al, 1986).

The splitting of 250°C internal friction maximum can be connected with moving twin boundaries

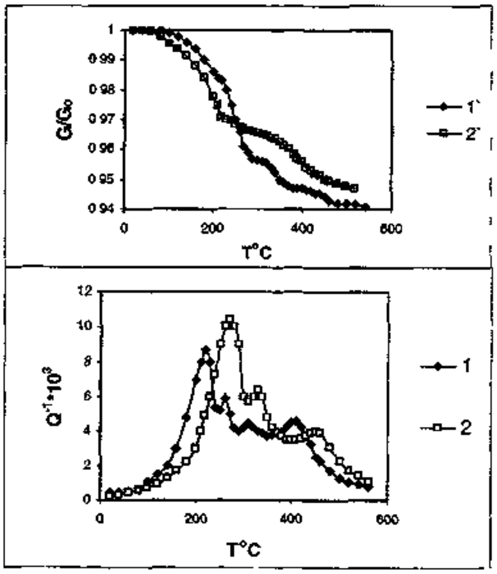


Figure2. Internal Friction and Shear Modulus: 1, 1' Initial State, f$_0$=5Hz. 2, 2' After annealing at 1000°C during lOOh, f$_0$=4.8Hz.

interacting with different types of solute complexes, which had formed during annealing. The origin of TEC hysteresis is unclear.

3. DISCUSSION

Thus, it was experimentally established that after high temperature annealing iron doped boron with hole concentration > 10^{17} sm"^{1} has changed its conductivity from p- to n-type, with the ten fold increase of electron carrier concentration and of electron mobility from 5 to 20 cn^V'sec"^{1}. Simultaneously microhar-dness and shear modulus have increased by 10-15%. Internal friction measurements of annealed samples showed that the main peak at 250°C attributed to twin boundary migration splinted and formed two peaks.

The observed changes may be explained by the annealing of planar defects and shifting of iron atoms, previously segregated on defects to electrically more active positions in solid solution. The splitting of internal friction maximum can be connected to moving twin boundaries interacting with different types of solute complexes.

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