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CREATION OF OXYGEN-ENRICHED LAYERS AT THE SURFACE OF GaAs SINGLE CRYSTAL

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Кулик М., Кобзев А.П., Мончка Д. E15-99-265
Создание обогащенных кислородом слоев на поверхности монокристалла GaAs

Исследованы оптические характеристики и глубинные профили элементов на (100) плоскости высокоомного некомпенсированного монокристалла GaAs, имплантированного ионами In. Результаты сравниваются с теми же характеристиками, полученными для исходных образцов. Оптические характеристики для всех образцов (имплантированных и неимплантированных, отожженных и неотожженных) были измерены эллипсометрическим методом. Глубинные профили элементов для тех же образцов получены с помощью методик RBS и NRA.

Показано, что послеимплантационный отжиг при температуре выше 600°C ведет к десятикратному увеличению содержания атомов кислорода в имплантированном слое по сравнению с неотожженным образцом. Толщина прозрачного слоя на поверхности монокристалла GaAs также увеличилась после имплантации ионами In и соответствующего отжига.

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Creation of Oxygen-Enriched Layers at the Surface of GaAs Single Crystal

The optical properties and the element depth profiles at the (100) plane high resistant and noncomposite GaAs single crystals implanted with In ions were investigated. The results have been compared with those obtained for virgin samples. The optic properties for all of the samples (implanted and not implanted, annealed and not annealed) have been measured using the ellipsometric method. The element depth profiles for the same samples have been obtained by the RBS and NRA techniques.

It has been shown that the post-implantion annealing at a temperature more than 600°C leads to a ten time increase in contents of oxygen atoms in the implanted layer with respect to the not annealed sample. The thickness of the transparence layer at the surface of GaAs single crystal increases also after implantation with In ions and subsequent annealing.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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INTRODUCTION

In the past ten years, the development of multylayer electronic system technology, used as laser junctions, caused an increasing interest towards the existing of oxygen-enriched layers in A_3B_5 compounds [1-4]. For these materials, specifically for GaAs and InAs, the experiments yielding information about the creation of stable chemical compounds on the surfaces of these single crystals are very important [5]. The great part of these works concerns the determination of external agents like ion implantation or light irradiation, which influence the oxidation process in surface layers [6-8].

With respect to the implantation, the parameters as an implantation dose, an energy, and an ion type are very important. These parameters influence the kinetics of oxidation of the surface layers and change the thickness, the oxidation rate, and the optical parameters of the native oxide layer as well as its chemical composition. The results of these experiments for GaAs implanted with Xe, Ar, and In ions have been presented in [9-10].

The aim of this paper is to investigate the influence of thermal annealing (known as RTA method) on the increasing content of oxygen atoms in the surface GaAs layers implanted with In ions. The RBS and NRA nondestructive techniques were applied to study the depth profiles of the dopands in the In-implanted GaAs. The change in optical parameters (refractive index and extinction coefficient) for the two annealing temperatures was studied using the ellipsometric method for one wavelength.

EXPERIMENTAL

Five samples of the high-resistant GaAs (100) crystal were investigated. Two of them were unimplanted and they served as reference samples. Three GaAs samples were irradiated with indium ions. The implantation was carried out on the UNIMAS79 implanter [11] at an energy of 200 keV and a dose of indium ions 10^{16} cm-^{2}. However, a current density was less than 0.1 $\mu A/cm^2$, therefore a so-called "cold" implantation took place. The vacuum in the chamber during the implantation was 10^{-6} Pa. The (100) plane was inclined with respect to the ion beam at an angle of 8° to avoid channeling of the implanted ions.

Two implanted samples were annealed using the RTA method at the temperatures 600 °C and 800 °C, respectively. The annealing time in the both cases was 40 sec and during this process each sample stayed in the stream of flowing Ar gas.

Then optical parameters (refractive index and extinction coefficient) for all of the implanted and not implanted samples were examined by the MAIE ellipsometric method [12] using the automatic ellipsometer EL11D with the wavelength λ=632.8 nm. The incident angles of the laser light beam with respect to the surface of the samples were changed from 65° to 72°.

The element depth profiling in the layer adjacent to the surface has been performed for all samples using the RBS method. Typical spectrum of the backscattered $^4He^+$ ions, obtained for implanted and annealed at 800° C GaAs sample, is shown in Fig.1. The depth distributions of indium atoms implanted into GaAs were determined by the RBS method for all of the implanted samples. It is shown that at the injection, the yield of $^4He^+$ ions scattered at the In atoms is rather low but the background is even lower. Thus, the concentration depth profile for In atoms can be obtained with the precision less than 5%.

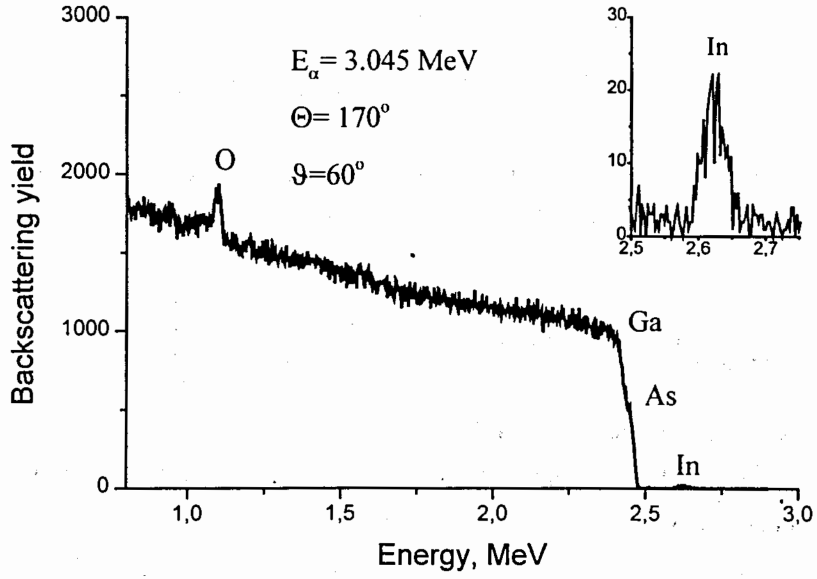

Fig.1. Backscattering spectrum for the implanted and annealed at 600° sample.

The determination of the depth profiles of oxygen atoms in the investigated samples was carried out using the ^{16}O $(\alpha,\alpha)^{16}O$ nuclear reaction that has a very narrow and a rather intensive resonance at the energy of 3.045 MeV [13]. As it can be clearly seen in Fig.1, for this incident energy the resonance stays just at the surface layer. Thus, we have a rather high yield of ions scattered by the oxygen atoms. For each sample some spectra were measured in the energy region from 3.03 MeV to 3.07 MeV with the step of 5 keV. The angle of the incident beam with respect to the surface of the samples was φ=30°. The depth profiles were obtained by processing the RBS spectra using the DVBS computing code [14].

RESULTS AND DISCUSSION

The treatment of the ellipsometric experiments was based on the 3-phase model of the samples (isotropic air area, plane-parallel layer, and homogeneous substrate). After [15], we have assumed that the oxygen-enriched surface layer is a transparent one (the extinction coefficient k_{ox}=0). This layer was called "a native oxide layer" and it is just the most interesting effect in this investigation. The ψ_e and Δ_e values have been obtained for eight incidence angles from the ellipsometric measurements. With these results, the following optical parameters for the investigated systems were calculated: n_{ox} and d_{ox} are the refractive index and the thickness of the native oxide layer; n_s and k_s are the refractive index and the absorption coefficient of the substrate, respectively.

Assuming a 3-phase system, four parameters n_{ox}, d_{ox}, n_s, and k_s have been obtained by the MAIE minimization method. Thus, the error function G(w) was described by the following equation:

$$G\left(\vec{w}\right)=\frac{1}{m}\sum_{i=1}^{m=8}\left[\left(\Delta_e(\varphi_i)-\Delta_T\left(\varphi_i,\vec{w}\right)\right)^2+\left(\psi_e(\varphi_i)-\psi_T\left(\varphi_i,\vec{w}\right)\right)^2\right], \quad (1)$$

where the vector W is determined as $\vec{w}\left[n_{ox},d_{ox},k_s,n_s\right]$.

The relationship between the ellipsometric angles ψ_T and Δ_T and Fresnel coefficients for the two polarizations R_p and R_s is described by the equation:

$$\operatorname{tg}\psi_T\, e^{i\Delta_T}=\frac{R_p(\lambda,\varphi,n_{ox},d_{ox},n_s,k_s)}{R_s(\lambda,\varphi,n_{ox},d_{ox},n_s,k_s)}, \quad (2)$$

where λ is the light wave length and φ is the incidence angle.

The optical constants of GaAs crystal were used for preliminaries estimations as initial data. The thickness of the native oxide layers obtained this way for different samples is shown in Table 1. It can be seen from the table that for the not implanted sample, the d_{ox} does not change after being exposed to air during one year. This conclusion is concerned to the annealed samples as well as to the not annealed ones. However, d_{ox} increased by about 35% and about 50% for the implanted samples and then annealed at 600°C and at 800°C, respectively.

Table 1. Thickness of native oxide layers [nm].

Exposureto air	GaAs not implanted			GaAs implanted		
	Before RTA	After RTA		Before RTA	After RTA	
		600^0	800^0		600^0	800^0
Initial	4.5	5.0	5.1	4.7	4.8	4.8
After one year	4.4	5.0	5.0	5.1	6.5	7.2

The refractive index n_s and the absorption coefficient k_s of substrate as well as refractive index n_{ox} of the native oxide layer increased after implantation of the samples with In ions. However, subsequent annealing almost restored the optical properties of the substrate (Table.2) but the refractive index of the native oxide layer did not change after the annealing, though its thickness increased.

The concentration depth profiles of all elements for the implanted and not anealed at the temperature 800°C sample is shown in table 3. The concentration In atoms at the surface reaches 0.5% and decreases to zero at the depth $4.29\text{x}10^{17}$ cm^{-2}. The atomic concentration of the oxygen has maximal value of 30% at the surface and falls to the zero at the same depth. Like this depth distributions all elements there are for the sample implanted and annealed at 600°C.

Table 2. Optical parameters for native oxide layers and substrates.

		n_{ox} ± 0.002	n	k
GaAs not implanted	before a year and without RTA	1.882	3.866± 0.008	0.298± 0.007
	after a year without RTA	1.881	3.866± 0.008	0.298± 0.007
	before a year and after RTA	1.881	3.866± 0.008	0.298± 0.007
	after a year and after RTA	1.881	3.866± 0.008	0.298± 0.007
GaAs implanted	before a year	1.995	4.363± 0.008	1.069± 0.002
	after a year	1.996	4.364± 0.008	1.067± 0.002
	before a year and after RTA 600	1.997	4.019 ± 0.004	0.342± 0.002
	after a year and after RTA 600	1.999	4.019 ± 0.004	0.339 ± 0.002
	before a year and after RTA 800	1.998	4.032± 0.003	0.349± 0.003
	after a year and after RTA 800	1.999	4.047± 0.002	0.341± 0.002

The depth profiles for all elements for implanted but not annealed sample is shown in Table 4. The depth profile of In atoms is almost the same as for the above mentioned samples but $5x10^{15}$ cm^{-2} oxygen atoms contain only there and they occupy the surface layer of $2.7x10^{16}$ cm^{-2} depth. The same number of oxygen atoms within the experimental errors is contained in the surface layer of virgin (not implanted and not annealed) sample.

Table 3. Element depth distribution for implanted and annealed at 800° C sample.

Depth [10^{16} atoms/cm^2]	Element concentration (at %)			
	In	As	Ga	O
2.7	0.33	34.43	34.43	30.81
4.1	0.41	36.89	36.89	25.81
5.5	0.44	43.13	43.13	13.29
10.8	0.47	43.76	43.76	12.02
21.5	0.48	43.82	43.82	11.88
32.2	0.43	43.86	43.86	11.86
42.9	0.29	44.35	44.35	11.01
50.0	0.0	50.00	50.00	0.00
50.0	0.0	50.00	50.00	0.00

The estimation by the RBS method of the thickness of the surface layer containing In atoms is about 90 nm immediately before and after RTA. This result agrees with calculations performed by computer simulation code TRIM, which gives the following results for the extrapolated range of In ions: Rp=62.0 nm and dRp= 26.9nm. It means also that the In depth distribution does not change essentially during the diffusion of oxygen atoms.

Table 4. Element depth distribution for implanted and not annealed sample.

Depth [10^{16}atoms/cm^2]	Element concentration [at. %]			
	In	As	Ga	O
2.7	0.39	40.57	40.57	18.48
4.1	0.55	49.72	49.72	0
5.5	0.51	49.75	49.75	0
10.8	0.53	49.73	49.73	0
21.5	0.54	49.73	49.73	0
32.2	0.49	49.76	49.76	0
42.9	0.33	49.84	49.84	0
50	0.00	50.00	50.00	0

One can see in Tab. 4. that after RTA annealing the presence of about 1 atom of O per 3 In atoms was found. This result can be explained by oxygen diffusion from air into the damaged by implantation layer of the single crystal. Also it is clear why the optical properties of the substrate have been highly increased after the implantation (Table 2). A damaged crystal lattice under implantation was restored by annealing (the optical properties have been restored up to almost virgin values) (Table 2). Because in the doping material In is present probably as a locally-formed InAs. Thus, the doped layer can be considered as a local mixture of these two crystal components with different crystal lattices.

Due to that fact, the local stress occurs, which is confirmed by the measurement of Raman spectra [16]. It might as well be a reason why the optical properties have not been totally restored after the annealing. The presence of the restored but not totally ordered structure of the doped crystal is a suitable material into which oxygen can diffuse from air.

Therefore, we can conclude that, as a result of the In ion implantation and subsequent annealing at the temperature higher than 600° C, a ten time increase in oxygen atom content occurs and the thickness of the transparent layer covering the surface of implanted GaAs single crystal is also increased.

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