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Application of the ion mixing method for doping near surface layers of the silicon single crystals

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Abstract. Penetration of alien atoms (Be, Al, Ni, Mo) into Si, diamond monocrystals substrates was investigated under Ar^+ ion bombardment of samples having thermally evaporated films of 30–50 nm. Sputtering was carried out using a wide energy spectrum beam of Ar^+ ions with mean energy 9.4 keV to dose D=l×l0^{16}–10^{19} ion/cm^2. Implanted atom distribution in the targets was measured by Rutherford backscattering spectrometry (RBS) of H^+ and He^+ ions with start energy of 1.6 MeV as well as secondary ion mass-spectrometry (SIMS).

During the bombardment, the penetration depth of Ar atoms increases with dose linearly. This depth is more than 3–20 times deeper than the projected range of bombarding ions and recoil atoms. This is a "ion mixing" process.

The analysis shows that the experimental data for foreign atoms penetration depth are similar to the data calculated for atom migration through the interstitial site in a field of internal (lateral) compressive stresses created in the near-surface layer of the substrate as a result of implantation. Under these experimental conditions atom ratio r_i/r_m (r_i - radius of dopant atom, r_m - radius of substrate atom) can play a principal determining role. Show that maximum penetration depth of the film atoms in the substrates may be determine by "isotropic model" under ion beam (with wide energy spectrum – polyenergy) irradiation of the "film–substrate" systems too.

1. Introduction.

Modern technology of doping materials by ion beams is mainly connected with the use of continuous ion fluxes having narrow energy spectrum and resemblance by their forms to the Gaussian distribution [1-4]. The ratio of the distribution of width on half-height (ΔE) to its mean magnitude (E) is of the order of 1–5%. Doping materials by ions with wide energy spectrum ($\Delta E/E$ = 30–50 %) is of certain scientific and practical interest because in this case the distribution of implanted atoms with the target depth could be changed [5]. However at present time, the data on modification of near-surface layers in structural materials under irradiation by ion fluxes of wide-spectrum energy are very scarce. We attempt to investigate the changes in distribution of dopant (Be, Al, Ni, Mo) with depth- $C(x)$- for some Si (110) and natural diamond – monocrystal substrates) in relation to the fluence (dose) of a polyenergetic argon ion beam.

2. Conditions and materials.

The irradiation was carried out using an instrument wich produces an ion beam with a Gaussian-type

energy distribution of argon ion beam within the energy range of $E = 4–13.7$ keV, at mean energy of $<E>=9.4$ keV [5]. The argon ions were directly implanted into targets made of Si, diamond and atoms of Be, Ni were inserted from sputtered films into substrates made of Si, natural diamond. For that purpose the films were bombarded by a polyenergetic beam of argon ions with mean energy of $<E> = 9.4$ keV and beam current density of $j = 5$ µA/cm^2.

The films of Be, Ni, Mo were deposited by means of thermal evaporation in vacuum ($p = 4\times10^{-4}$ Pa). Thickness of the wall to (X_t) was chosen to be greater then the penetration depth of the argon ions ($X_t \approx R_p$) and was of $X_t = 30–50$ nm.

The distribution profile of inserted atoms with depth was determined by two methods: secondary ion (Ar$^+$ and O$^+$) mass spectrometry (SIMS) with ion energy $E = 4.6$ keV using the PHI-600 device and by Rutherford back-scattering (RBS) of fast ions (H$^+$ and He$^+$) with initial energy of $E = 1.6$ MeV. The depth resolution errors of RBS method was not more than ± 5 nm, of SIMS method ± 1 nm. The relative concentration errors of RBS method was not more than ± 0.1 at %, of SIMS method $- \pm 10^{-2}$ at %.

As parameter of change of conductivity of Si and diamond doped surfaces are investigated to change of spectra of absorption of optical radiation in an interval of lengths of waves 0.1 - 1.4 µm on devices СФ – 46 and Carry – 1000.

3. Experimental results.

3.1. Implantation of Ar atoms

Recovered distribution profiles - $C(x)$ of Ar into Si are presented in Figure 1. The analogous dose relationships for inserted argon distribution were obtained with Al and Si. The results of experiments to determine the most probable (X_p) and maximum (X_m) penetration of argon ions into Be, Al and Si are presented in the Table 1. As can be seen in Figure 1 the accumulation of Ar in Si is changed with the increase of fluence. With low fluencies, the maximum argon concentration is near the projective range (R_p = 12 nm with E = 10 keV) and amounts to X_p =10–20 nm. When the fluence exceed $D = 7\times10^{21}$ m^{-2}, the overall content of Ar drops, gas concentration near the irradiated surface being halved. This probably is connected with gas release through discharge channels created in the process of bombardment. With fluence increase, the location of maximum Ar concentration in Si shifts in depth to X_p= 35 nm. It's important to emphasize that with fluence increase the depth of argon atom maximum penetration (X_m) also increased. As can be seen from the table$_5$ maximum penetrations (X_m) for atoms of Ar are, in the case of penetration into Si, X_m= 82 nm ($D = 1\times10^{22}$ m^{-2}), in Al X_m = 58 nm ($D = 1.5\times10^{22}$ m^{-2}), and in Si X_m = 88 nm ($D = 1.4\times10^{22}$ m^2).
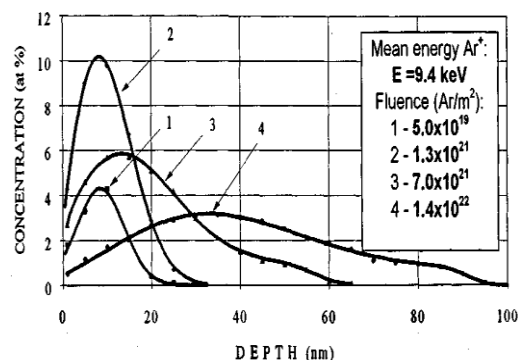

Figure l. Distribution of implanted Ar$^+$ ions into Si target with mean energy $<E>=9.4$ keV and fluence
   D: 1– 5×10^{19} ion/m^2, 2 –1.3×10^{21} ion/m^2, 3– 7.0×10^{21} ion/m^2, 4– 1.4×10^{22} ion/m^2

3.2. Implantation of atoms from films into substrate.

The typical distribution of atoms from surface films in the substrate after bombardment of the film by Ar$^+$ ions is presented in Figure 2 for the case of Ni implantaion into Si. As can be seen from Figure 2, a considerable penetration of Ni atoms was observed up to depths of $X = 5$–10 nm, i.e. to depths 3–5 times higher than the range of argon ions ($R_p = 3$ nm) or the range of primary knock-on atoms of nickel into Si ($R_p = 3.5$ nm). Maximum penetration of Ni atoms into Si was established at depths exceeding $X = 15$–20 nm.
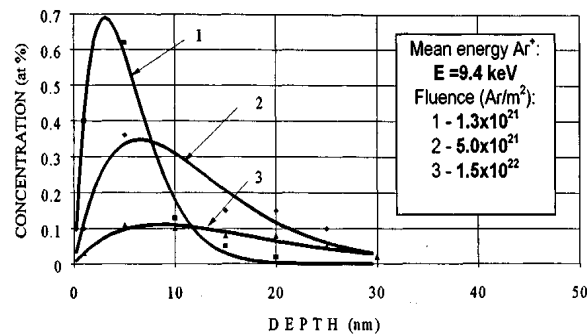

Figure 2. Distribution of implanted Ni atoms into Si substrate under irradiation by Ar$^+$ ion beam with mean energy $\langle E \rangle = 9.4$ keV and fluence D: 1- 5×10^{19} ion/m^2, 2- 1.3×10^{21} ion/m^2, 3- 5.0×10^{21} ion/m^2, 4- 1.5×10^{22} ion/m^2

As can be seen from data presented in the Table 1, analogous penetration of Be, Ni and Mo atoms was observed from the film into the substrates of Al, Si and diamond. Detailed analysis of Be atom distribution in diamond revealed that with agron ion fluence $D = 1 \times 10^{22}$ m^{-2} Be concentration in the near-surface layer of diamond was $C(X=0) = 3$ at %. This value is changed very slightly up to $X = 20$ nm. At the depth of $X = 70$–90 nm the concentration of Be was 0.5 at%. Then it was falling down and reached the magnitude of 0.1–001 at% by the depth of $X > 100$ nm.

Table 1. Depth of implanted Ar$^+$ ions and film atoms

Dopant atoms	Substrate	Fluence, $\times 10^{21}$ m^{-2}	Depth, nm	
			X_p	X_m
Ar	Be	0.5	3	33
		1.0	25	48
		5.0	31	63
		10.0	48	82
	Al	1.3	18	45
		5.0	22	40
		15.0	35	58
	Si	0.5	7	23
		1.3	10	26
		7.0	26	42
		14.0	49	88
Be	Al	5.0	26	42
	Si	10.0	31	68
	diamond	10.0	50	113
	Al	7.0	21	45

Ni	Si	10.0	9	25
	Si	7.0	12	26
Mo	diamond	10.0	30	55

3.3. Change of a transmission spectrum. As the diamond in an initial condition has the large specific electro resistance and during it doping under a Ar$^+$ ion beam probably accumulation of a electrical charges. Trial doping is carried out on samples from silicon organic polymer of a material with smaller electro resistance and having the optical characteristic close to diamond.

On Figure 3 the results of measurement of transmission spectra of samples, in an initial condition irradiated with Ar$^+$ ions with a different doze of an irradiation and doping of the Be atoms with concentration up to 1 at% are submitted. These spectra show decrease of a transparency of samples with increase of a doze of an irradiation and doping of Be atoms in the field of lengths of waves up 400 to 900 nm.
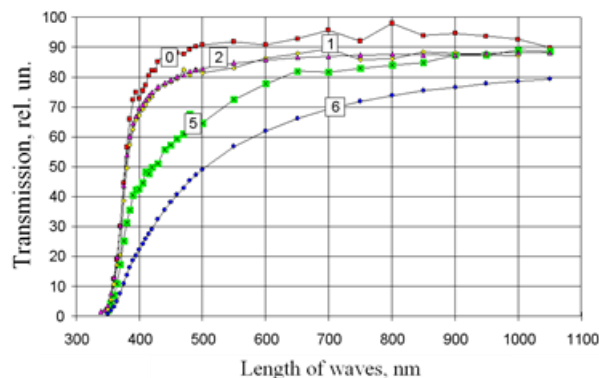

Figure 3. Change of a transmission spectrum of the silicon organic polymer samples at an irradiation by Ar ions and introduction of the Be atoms, irradiation doze of samples *D*: 0- in an initial condition; 1- $D = 7 \times 10^{20}$ m^{-2}; 2- $D = 1 \times 10^{20}$ m^{-2}; 5- $D = 1.3 \times 10^{21}$ m^{-2}; 6- Be atoms and $D = 1.7 \times 10^{21}$ m^{-2}

On Figure 4 the transmission spectra of diamond in an initial condition (1) irradiated Ar by ions up to a doze $D = 1{,}3 \times 10^{21}$ ion/m^2 (2) and doping by Be atoms (3) are submitted. As visible from figure the irradiation of the sample by Ar$^+$ ions is reduces a transparency of diamond sample almost twice in an interval of lengths of waves up 225 to 190 nm. Doping of diamond by Be atoms essentially changes dependence of a transparency of diamond on length of a wave, i.e. the curve of dependence has concave character, on length of a wave 226 nm the abnormal absorption of optical radiation is observed, on a length waves site 265 – 285 nm are observed oscillation in a transparency of the diamond sample.
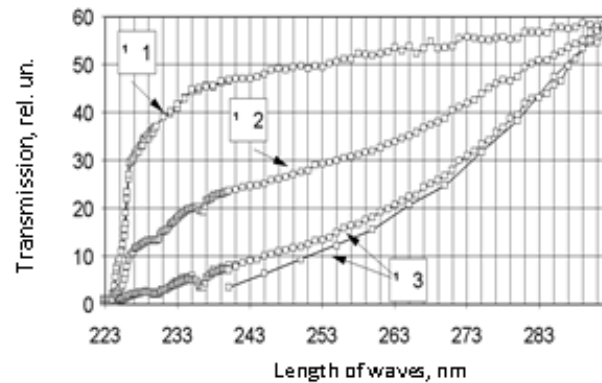
Figure 4. Change of a transmission spectrum of the diamond
samples at an irradiation by Ar ions and introduction of the Be
atoms, irradiation doze D of samples: 1- D=0 in an initial condition;
2- $D = 1{,}3 \times 10^{21}$ m^{-2}; 3- Be atoms and $D = 1.6 \times 10^{21}$ m^{-2}

4. Discussion

The Table 1 presents the basic results of the experiments to investigate the dynamics of Ar, Be, Ni atom penetration Be, Al, Si and diamond under bombardment of samples by polyenergetic Ar$^+$ ions beam - with different fluences. The comparison of the experimentally gained values concerning Ar$^+$ ions ranges in Be, Al, and Si with the calculated data on these ranges (R_p) for monoenergetic beams (presented, for instance, in ref. 6) shows that in the case of irradiation by Ar$^+$ polyenergetic beam, penetration of Ar atoms to depths considerably large then R_p can be observed. This could be connected with the fact that the beam includes Ar ions having energy higher than mean value. As can be seen in Figure 5, the magnitude of Ar$^+$ ion penetration – $\langle X_p \rangle$ (where $\langle X_p \rangle$ is mean value from $C(x)$ - $C(x)_c$, $C(x)$ is the experimental distribution profile of atoms, $C(x)_c$ is the calculated distribution profile of atoms for a polyenergetic beam) into Al, Si, Be increases linearly with fluence as in [3,4].
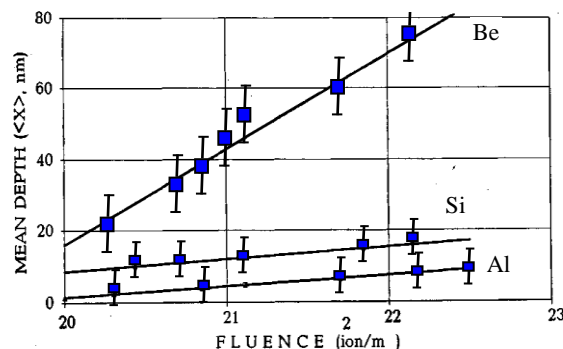

Figure 5. The influence of implanted Ar$^+$ ions fluence on $\langle X_p \rangle$ range

In this case, X_p increases in the order Al - Si - Be at all fluences. It is important to emphasis that the ratio between the radius of Ar atom and the radius of Al, Si, Be atoms (0.134 : 0.164 : 0.17 nm) as well as Young's moduli of Al, Si, Be (70 : 160 :310, GPa) increase in the same order. The analogous effect of "deep action" can also be observed under implantation into the base layers of atoms films by ions of argon. Atoms of Be and Ni penetrate into Al, Si, and diamond base layers to the depths which exceed the ranges of primary knock-on atoms. Judging by primary knock-on atom energy magnitudes presented in the Table 1 the process of the implantation by Ar ions is accompanied by knock-on atoms of films in the regime of dynamic mixing [2] to considerable depths. Analysis of the film atom

maximum penetration (the results ar resented in Figure 6) shows that the case atom penetration depth also increases with the ratio of implanted atom radius (r_i) to substrate atom radius (r_m).
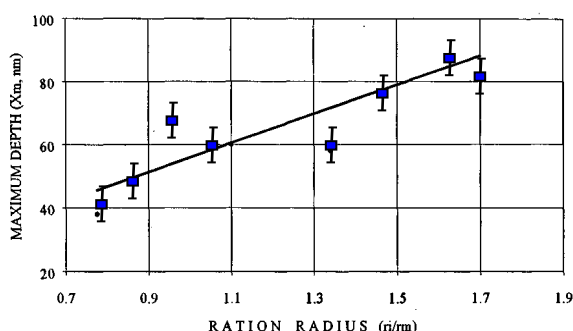

Figure 6. The influence of r_i:r_m on the maxiumum range(X_m) of dopant atoms

To reveal the mechanism of Ar ion and Be, Ni atom deep penetration into the material, the calculation of distribution profiles of inserted atoms   was conducted with consideration of the "deep action" mechanisms outlined by Yu. Martynenko [7]. The closest agreement with the experimental data was obtained in the course of assessments concening inserted atom migration through the interstitial site in a field of internal (lateral) compressive stresses created in the irradiated material near-surface layer as a result of implantation [8]. In this case the penetration of the atom being implanted greater than the expected depth of penetration owing to radiation enhanced diffusion. Here $\alpha = (BN_0 e/D)^{1/2}$. N_0 is the specific density of the matrix material, B – is a parameter of the radiation enhanced diffusion, D is a coefficient for thermal diffusion, e = 2.718...., α = 10...16 for the case using typical parameters characterizing irradiation, matrix material and inserted atoms. As show experiments doping by film atoms various substrates [9] maximal depths of introduction more precisely can be described within the framework of isotropic ion mixing model [10]. However for systems "film-substrate" it is necessary to take into account an opportunity of physicochemical interaction between their atoms. For example result of a physicochemical analysis of the «Be-film – diamond-substrate» system it has been established that peak mutual penetration of atoms depends on their electronegativities χ, or more precisely on the electronegativity difference for film- and substrate-atoms $\Delta\chi$ [11]. The value of X_m/R_p decreases with strengthening the physicochemical interaction of atoms (with an increase of $\Delta\chi$).

5. Conclusion
1. Irradiation by an Ar ion by polyenergetic beam revealed the penetration of argon atoms to depths 3–10 times greater then the calculated ranges of monoenergetic beams of Ar^+ ions.
2. The ion mixing of Be, Ni and Mo film atoms allows to obtain considerable penetration of these atoms into Al, Si and diamond substrates, the doped layer depth being 20 and more times greater than the culculated projective range of the recoil atoms.
3. The penetration depth of the film atoms into a substrate (X_m/R_p) at a fixed fluence and energy-release in a sample depends on the reduced mass of a beam and a target, the energy reported to recoil atoms, and physicochemical interaction of atoms (for example, electronegativity difference).

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