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PROPERTIES INVESTIGATION OF THIN SILICON NITRIDE LAYERS SYNTHESIZED BY ION IMPLANTATION

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Structure and phase transformations of Si irradiated by nitrogen ions of 60 keV with doses from 5×10^{15} ions · cm^{-2} to 6×10^{17} ions · cm^{-2}, and ion current density 20 μA · cm^{-2} have been studied by transmission electron microscopy and ir absorption techniques. The samples were annealed in vacuum from 600°C to 1100°C.

1. INTRODUCTION

The synthesis of Si_3N_4 layers on Si by ion implantation technique has been reported earlier.[1–9] However, the results on recrystallization temperature of Si_3N_4 layers and identification of the formed phases on the basis of optical and structural data are not sufficient, sometimes controversial and demand further investigations.

The present paper reports the basic results of the study of structure and phase transformations in Si crystals, irradiated with different nitrogen ion doses, as well as the data of their isochronal and isothermal annealing. The studies have been carried out by transmission electron microscopy and ir-absorption techniques.

2 EXPERIMENTAL PROCEDURE

Si original samples were cut in (111) plane, mechanically and chemically polished. The initial dislocation density in the samples was 10^2 to 10^4 cm^{-2}. Irradiation was performed by 60 keV nitrogen ions at room temperature (no special precautions were taken against heating of the samples during irradiation) at ion current density, $j = 20$ μA · cm^{-2} with integral doses from 5×10^{15} ions · cm^{-2} to 6×10^{17} ions · cm^{-2}. The samples were annealed isochronally in vacuum (better than 5×10^{-6} Torr) in the temperature range of 600°C to 1100°C, $\Delta T = 100$°C, $t = 30$ min and isothermally at 1100°C from 5 to 60 minutes, $\Delta t = 5$ min.

For structure investigations samples were chemically etched in the mixture of nitric and hydrofluoric acids.

3 EXPERIMENTAL RESULTS AND DISCUSSION

Irradiation of Si crystals by nitrogen ions in the above dose ranges have been found to cause amorphization of the near-surface region of a crystal. At doses of 0.05×10^{17} to 1×10^{17} ions · cm^{-2} the diffraction pattern coincides with that of Si amorphous film, obtained by thermal sputtering in vacuum. Two diffusion rings with the effective interplanar distances $d_1 = 3.22$ Å and $d_2 = 1.78$ Å are observed.

At doses higher than 1×10^{17} ions · cm^{-2} the character of the diffraction pattern considerably changes due to an essential growth of the phase Si_3N_4. Two diffusion rings with the effective interplanar distances $d_1 = 3.17$ Å and $d_2 = 1.26$ Å are observed. It should be noted that the difference between the d_{eff} values of the present paper and those in Ref. 10 ($d_1 = 3.9$ Å and $d_2 = 1.35$ Å) for amorphous Si_3N_4 is apparently due to a complex structure of the volume being probed which includes regions of amorphous Si and non-stoichiometric complexes like Si_xN_y along with the precipitates of the phase Si_3N_4.

Annealing study of irradiated samples has shown that recrystallization of the layers, implanted with nitrogen ions at a dose of 5×10^{15} ions · cm^{-2}, occurs epitaxially in the temperature range of 600°C to 700°C. A complex structure formation in which amorphous layer turns out to be buried should be expected at the given dose of irradiation. Crystalline state of the sample surface plays an orientational role upon recrystallization of irradiated Si.

At high ion doses (0.1×10^{17} ions · cm^{-2} to $1 \times$

10^{17} ions · cm^{-2}) recrystallization temperature increases up to about 700°C to 800°C. The growth of recrystallization temperature of amorphous Si may be associated either with stabilization of radiation defects, by nuclei of the phase Si_3N_4 [11] and molecular complexes Si_xN_y, or with the formation of compound stable defects, which include molecules of their compounds. The diffraction pattern in this case exhibits a polycrystalline surface layer of Si. The traces of Si_3N_4 were not observed even at an annealing temperature of 1000°C.

The diffraction pattern from the amorphous structure remains the same up to an annealing temperature of 900°C whereas annealing at 1000°C leads to an amorphous layer recrystallization at a dose of 4×10^{17} ions · cm^{-2}. This phase is identified as α-Si_3N_4 (Table I). Substrate plays an important role in determining the recrystallization temperature. In our case, the layers, separated from the matrix by chemical etching, remained amorphous after annealing to 1000°C.

Three diffusion rings with the effective interplanar distances $d_1 = 3.9$ Å, $d_2 = 2.12$ Å and $d_3 = 1.22$ Å were observed on the diffraction pattern. Recrystallization temperature of 1000°C is characteristic of the samples irradiated with nitrogen ions at a dose of 6×10^{17} ions · cm^{-2}. Lines of only α-phase of Si_3N_4 were observed on the diffraction pattern. The layers separated from the matrix by chemical etching remained amorphous at the given annealing temperature. Mixture of α- and β-phases of Si_3N_4 have been observed for the given nitrogen ion dose in Ref. 6.

Previously[14] it was pointed out that α-phase usually forms in the presence of excess oxygen. The type of a phase formed during creation of Si_3N_4 layers by ion implantation technique depends not only upon the presence of free silicon or oxygen but on irradiation conditions (the target temperature,[9] ion current density, vacuum conditions in the accelerator chamber) as well.

Isothermal annealing of Si, irradiated by nitrogen ions at a dose of 6×10^{17} ions · cm^{-2} at 1100°C from 5 to 60 minutes ($\Delta t = 5$ min) was performed in order to clear out the nature of nucleation centres and the dynamics of Si_3N_4 crystal growth. It was found that following a 5-min annealing interval gave (Figure 1a) crystalline inclusions of the α-Si_3N_4 phase appearance in Si_3N_4 amorphous film in the form of spherulitic and linear dendrites (the shape of the dendrites being shown in Figures 1 and 2) with the size up to 2 μm and 2 to 6 μm, respectively. The observed density of the spherulites was 1×10^7 cm^{-2} to 10×10^7 cm^{-2} and that of linear dendrites was 1×10^3 cm^{-2} to 10×10^3 cm^{-2}. Annealing for 30 min gave a continuous polycrystalline layer of α-Si_3N_4 whereas 60-min annealing only caused an enlargement of the crystallites.

According to the model proposed in Ref. 6 the traces of dislocation loops introduced into the matrix owing to the coagulation of point defects, at the initial stage, afterwards become decorated by

TABLE I

Interplanar distances of Si_3N_4 layers prepared by different techniques

Data of this paper		Ref. 6	Ref. 5	Ref. 12		Ref. 13		*hkl*
d, Å	*hkl*	*d*, Å	*d*, Å	*d*, Å α-Si_3N_4	*d*, Å β-Si_3N_4	*d*, Å α-Si_3N_4	*d*, Å β-Si_3N_4	
6.694	100					6.68	6.55	100
4.283	101	4.31	4.1	4.31		4.28		101
3.858	110	3.80		3.88	3.79	3.86	3.80	110
3.341	200	3.31		3.35	3.29		3.29	
3.150	111	3.15						
2.873	201	2.88		2.88				
2.584	102	2.59		2.59	2.66	2.53		112
2.529	210	2.54	2.51	2.54	2.49	2.48	2.48	300
2.311	112	2.33		2.31	2.31			
2.153	202	2.18	2.18	2.15		2.15	2.17	212
2.078	301		2.10			2.07		301
1.882	212	1.92	1.96	1.94	1.90	1.94		220
1.862	310							
1.802	103							
1.770	311							
1.512	213							

FIGURE 1 Isothermal annealing of Si irradiated by nitrogen ions to a dose of 6×10^{17} ions · cm^{-2}, $T_{ann} = 1100°C$, $\Delta t = 5$ min.

nitrogen atoms can be thought to be the nucleation centres of the spherulites, and those of linear dislocation segments which existed in the layer before irradiation can be considered to be the nucleation centres of the linear dendrites.

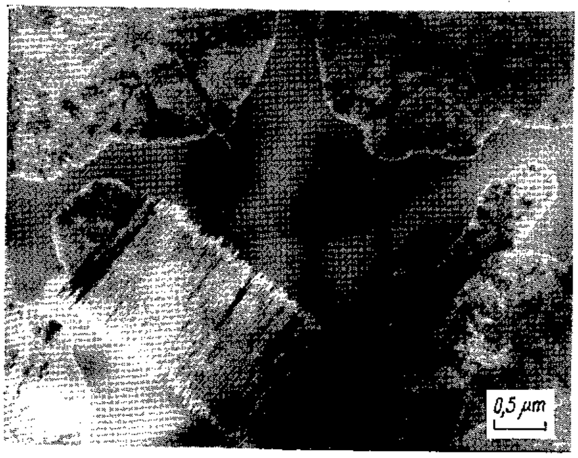

FIGURE 2 Linear dendrite αSi_3N_4 in Si irradiated by nitrogen ions to a dose of 6×10^{17} ions · cm^{-2}, $T_{ann} = 1100°C$, $\Delta t = 15$ min.

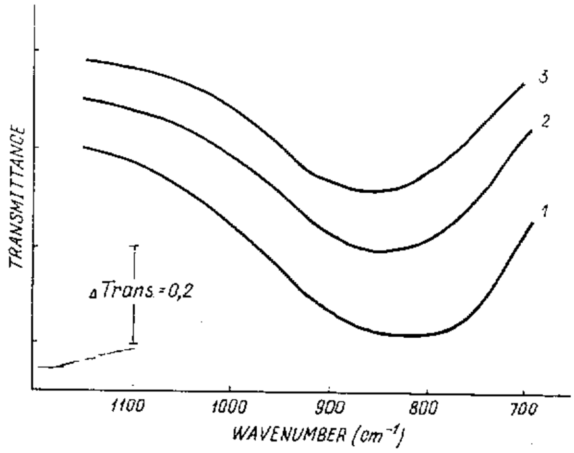

FIGURE 3 IR-spectrum of transmission for Si irradiated by nitrogen ions to a dose of 4.7×10^{17} ions · cm^{-2}. Before annealing (1), $T_{ann} = 700°C$ (2), $T_{ann} = 900°C$ $t = 30$ min (3).

IR-transmission spectrums were recorded on Model 180 Perkin-Elmer Spectrometer at room temperature in the wave range of 1200 to 200 cm^{-1}. Figure 3 shows transmission spectrum of Si crystals irradiated by nitrogen ions at a dose of 4.7×10^{17} ions · cm^{-2} before (curve 1) and after annealing at 700°C and 900°C (curves 2 and 3, respectively).

An unannealed sample showed a broad asymmetric band with the absorption maximum near 800 cm^{-1}. Annealing at 700°C and 900°C leads to an essential increase of transmission in the range of the long waves and to the band's symmetrization. The band's maximum being shifted towards 850 cm^{-1}. A similar broad structureless band was

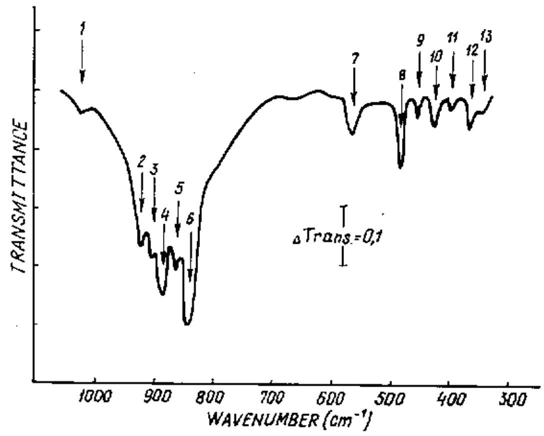

FIGURE 4 IR-transmission spectrum for Si irradiated by nitrogen ions to a dose of 4.7×10^{17} ions · cm^{-2}, $T_{ann} = 1100°C$, $t = 30$ min.

TABLE II
Absorption bands in the ir-transmission spectra

Data of this paper		Data of Ref. 15	
No.	ν, cm^{-1}	α-Si_3N_4 (ν, cm^{-1})	β-Si_3N_4 (ν, cm^{-1})
		1045	
			1040
1	1030		
		985	
			980
2	927		
			906
3	906		
		896	
4	885		
5	862	858	
6	847		
		750	
		684	
			680
		676	
		668	
		660	
		605	
			580
7	570		
		510	
		501	
			496
		493	
8	485	488	
9	460	461	
			445
10	432		
11	405	403	
12	370	375	376
13	355	352	
		305	

observed by other authors[15] in the spectrum of Si_3N_4 amorphous films. Annealing at 1100°C considerably alters the 850 cm^{-1} spectrum, where a well-defined structure appears. Furthermore, a series of less intense bands are observed in a more distant region of 700 to 200 cm^{-1}.

Figure 4 shows in detail the transmission spectrum of the sample annealed to 1100°C. The positions of the absorption bands 1 to 13 are indicated in Table II along with the positions for absorption bands of α- and β-phases of Si_3N_4 from Ref. 15.

A comparison of α-Si_3N_4 spectrum[15] with that of ion-synthesized compound exhibits a good coincidence in the long-wave region. However, the most intense bands 2, 4 and 6 are hardly comparable to the spectrum of α- or β-phase of Si_3N_4. It should be noted, however, that the bands, 927 cm^{-1}, 885 cm^{-1} and 847 cm^{-1} with similar intensity relationship were observed in spectra of nitrogen-implanted Si after proper thermal treatment performed by other authors.[7,8] Thus, in spite of some difficulties which arise at interpretation of the absorption spectrum of the synthesized compound partly due to the fact that the process of a compound formation by ion implantation takes place in extremely non-equilibrium conditions, it should be identified as α-Si_3N_4. The presence of carbon in the near-surface region of the crystal, which enters the sample surface from the residual gases in the accelerator chamber and later is implanted deep inside owing to recoil effects may possibly affect the position of bands 2, 4 and 6.

Synthesis of Si_3N_4 on Si substrate preliminarily amorphisized by Si^+ ions was additionally performed. In this case the spectrum taken directly after nitrogen ion implantation is similar to that of the sample without preliminary amorphization but annealed to 700°C. This implies that in the case of amorphous target the synthesized layer obtained was more perfect. At higher annealing temperatures the difference in the spectrum was not observed.

4 CONCLUSIONS

A considerable increase in the magnitude of the new phase by irradiation is observed in the ion dose range of 1×10^{17} ions·cm^{-2} to 4.7×10^{17} ions·cm^{-2}.

Recrystallization temperature of the irradiated layer grows with irradiation dose from 600–700°C at a dose of 5×10^{15} ions·cm^{-2} to 700–800°C at doses of $0.1–1.0 \times 10^{17}$ ions·cm^{-2}, to 900–1000°C at a dose of 4.7×10^{17} ions·cm^{-2} and to 1000–1100°C at a dose fo 6×10^{17} ions·cm^{-2}. Recrystallization of the layers irradiated with a dose of 5×10^{15} ions·cm^{-2} occurs epitaxially to the matrix.

Upon recrystallization of the layers irradiated with ion doses in the range of 0.1×10^{17} ions·cm^{-2} to 1×10^{17} ions·cm^{-2} polycrystalline silicon layers form.

As a result of recrystallization of the layers irradiated with ion doses in the range of 4.7×10^{17} ions·cm^{-2} to 6×10^{17} ions·cm^{-2} polycrystalline α-Si_3N_4 layers form. The nuclei of the phase α-Si_3N_4 have the form of spherulitic and linear dendrites.

Three intense absorption bands ($927\ cm^{-1}$, $885\ cm^{-1}$ and $847\ cm^{-1}$) are observed on ir-spectrum of transmission from the samples irradiated with a dose of 6×10^{17} ions $\cdot$ cm^{-2} having no analogues in the spectrum from Si_3N_4, obtained by other technique.

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