MODIFICATION OF AMORPHOUS Si-RICH SiN_x MATRIX BY IRRADIATION WITH SWIFT HEAVY IONS

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The effects of 200 MeV-Xe^+ irradiation with fluencies of (10^9-10^{14}) cm^{-2} on the phase-structural transformation of Si-rich SiN_x film deposited on Si substrate by LPCVD have been reported. It has been shown from RS data that the SHI irradiation results in the dissolution of amorphous Si nanoclusters in nitride matrix. It has been shown, too, that the SHI irradiation leads to quenching a visual PL from nitride films. It can be suggested that SHI irradiation before annealing can result in the formation of Si phase in nitride matrix with less Si excess in comparison the ordinary thermal annealing.

Introduction

Swift heavy ion (SHI) projectiles can produce point defects, defect clusters and ion latent tracks - extended damage regions along ion trajectories - in an irradiated target. Ion tracks were first observed in nuclear fission reactors [1] and since then they have been widely studied due to their growing list of technological applications.

It is possible to modify thin films of insulators by means of SHI irradiation. Owing to a different chemical reactivity than virgin matrix, the latent track regions in SiO_2 can be transformed into nano- or microchannels by means of etching in hydrofluoric acid (HF) solutions [2-4]. Another promising field is a possibility for controlling the shape and size of nanoclusters embedded in dielectric matrix by means of SHI irradiation. The authors of Refs [5-8] have reported a shape transformation of Ag, Au, Co and InAs nanoparticles embedded into amorphous SiO_2 films from spherical one to conical or elongated along the SHI beam direction. A new wave of interest in studying the SHI-SiO_2 interaction is due to a possible usage of SHIs for the creation of Si-based light-emitting nanostructures via SiO_2 disproportionation in the ion tracks [9, 10] or via a formation of Si nanoclusters in sub-oxide (SiO_x) due to the ion beam induced separation of semiconductor phase from oxide phase [11]. While most of the previous studies have concentrated on SHI induced modifications of SiO_x thin films, the effect of ion irradiation on the Si-nanostructures embedded in *a*-SiN_x matrix has not been studied. Silicon nitride is one of the most important dielectrics in the current planar silicon technology. Amorphous silicon nitride films are used in the integrated circuit production as insulating and passivating coatings due to their prominent dielectric and thermal properties in combination with chemical inertness. In the last decade, the light-emitting properties of silicon nitride and its potential application as a light source are in focus of scientific interest.

In this paper, we have studied the SHI irradiation effects on the structural and optical properties of Si-riched SiN_x layers deposited on Si substrate.

Experimental

The Si-rich nitride film was deposited on n-type (100)-oriented Si substrate by low pressure chemical vapor deposition at 800°C using the gaseous mixture of dichlorosilane (SiH_2Cl_2) and ammonia (NH_3) as precursors. The SiH_2Cl_2/NH_3 relation was changed during a deposition process in order to form nitride film consisted of two layers with different stoichiometric parameter “x”. It was made for the sake of comparison the effect of annealing and SHI irradiation on the SiN_x matrices differed in the level of excessive (in comparison with stoichiometry) Si content. The refractive index of nitride film measured by laser ellipsometry was equal to 2.22. The samples with the size of 1×1 cm^2 were cut out of SiN_x/Si wafer and irradiated at the cyclotron DC-60 (Astana, Kazakhstan) with 200 MeV Xe ions in fluence range of (10^9–10^{14}) cm^{-2}. A part of the samples was annealed in nitrogen ambient at 1100 °C during 60 min in a resistance furnace. The composition of as-deposited SiN_x film was determined by Rutherford backscattering spectrometry using 1.3 MeV He^+ ions from HVE accelerator. The amount of excessive silicon Si_{exc} in SiN_x layers was calculated by the equation from [12]:

$$Si_{exc.} = \frac{Si_{at.\%}}{Si_{at.\%}+N_{at.\%}} - \frac{3}{7}. \qquad (1)$$

The structural properties of nitride samples were investigated using Raman scattering (RS) technique on both as-deposited and irradiated samples. RS measurements were carried out by micro-Raman setup Nanofinder. The samples were excited with a laser beam (λ = 355 nm) and the scattered light was detected in back-scattering geometry at room temperature. The spectra of photoluminescence (PL) were registered at room temperature in the spectral region of 350 – 800 nm using a He-Cd laser source with λ= 325 nm. The structural transformations in SiN_x layer after irradiation and annealing were investigated by transmission electron microscopy in the “cross-section” geometry (XTEM) using a Hitachi H-800 microscope operated at 200 keV.

Results and Discussion

Figure 1 shows RBS spectrum and calculated depth profile of the nitride film composition. One can see that there are two regions at the dependence “Si and N atoms concentration – nitride film’s depth” differed in Si/N relation. A subsurface nitride layer

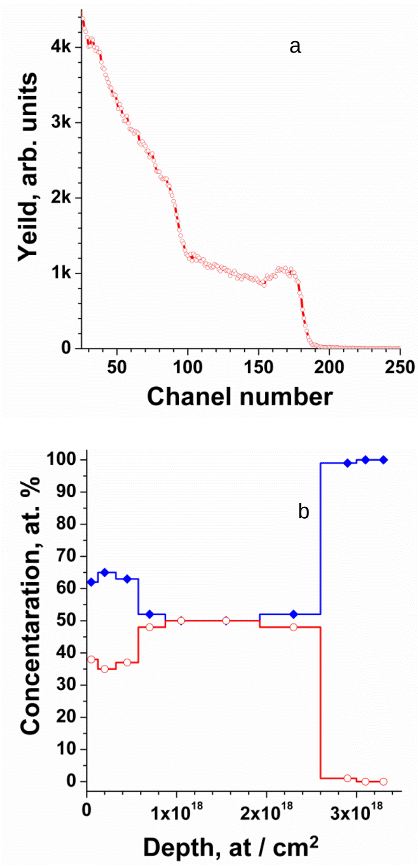

Fig. 1. RBS spectrum of as-deposited SiN_x film (a) and depth profile of Si (-♦-) and N (-○-) concentrations (b)

is characterized with "x" of 0.54 ($SiN_{0.54}$). It corresponds to the amount of excessive silicon (Si_{exc}) ≈22 %. Underneath that subsurface region the layer with "x" of 1.0 ($SiN_{1.0}$) is situated. The level of excessive Si in this region amounts to ≈7 %.

The existence of two layers in the nitride film under investigation is proved by TEM data. Figure 2 depicts TEM "cross-section" images of the as-deposited sample as well as the samples after annealing and after Xe^+ ions irradiation followed by annealing. Two layers are clearly seen on the TEM-image of as-deposited nitride film: a subsurface layer with the thickness of ~80 nm and under that - the second one with the thickness of ~290 nm (Fig. 2A).

Annealing results in the formation of the inclusions of dark contrast in the subsurface nitride layer. Taking into account the substantial level of excessive Si in this region (≈22 %) one can conclude that these inclusions are Si precipitates. It is well known that high-temperature thermal annealing of Si-rich SiN_x films leads to the formation of Si nanocrystals embedded in nitride matrix. It should be noted the absence of any precipitation in the second nitride layer situated deeper with the level of excessive Si ≈7 %.

Combined influence of the SHI irradiation at first and annealing afterwards has been shown in Fig. 3c. It should be marked that the dark inclusions are getting bigger in comparison with the sample after annealing only. The thickness of the layer with Si precipitates is equal to ~100 nm in comparison with ~80 nm for the annealed sample without SHI irradiation. In addition, the third layer with dark contrast appears in TEM-image of the SHI-irradiated and annealed nitride film. It is situated under the layer with precipitates and characterized with the thickness of ~100 nm. We can suggest that SHI irradiation induces an additional phase separation in the nitride layer with relatively low Si excess. It can be expected that additional SHI irradiation before annealing can result in the formation of Si phase in nitride matrix with less Si excess in comparison with the ordinary thermal annealing.

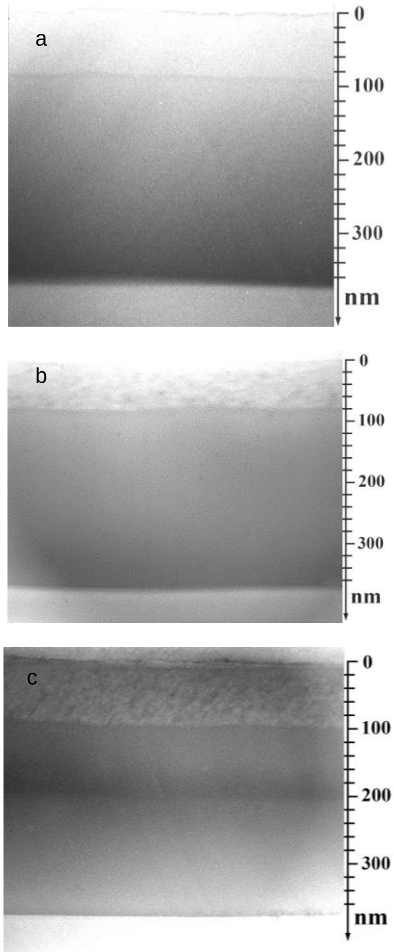

Fig. 2. XTEM images of as-deposited nitride film (a), nitride film after annealing at 1100°C, 60 min (b) and after irradiation with Xe^+ ions (200 keV, $1{\cdot}10^{14}$ cm^{-2}) followed by annealing (c)

Figure 3 shows RS spectra of as-deposited nitride sample and the samples after the irradiation with a number of swift Xe^+ ions fluencies.

One can see in the RS spectrum of the as-deposited nitride film a broad band with maximum at 480 cm^{-1}. It is a signature of Si amorphous phase. SHI irradiation with the fluencies of 10^9 and 10^{12} cm^{-2} results in the decrease of the band intensity. The fluence increasing to 10^{14} cm^{-2} leads to the whole disappearance of the band from Si amorphous phase in RS spectrum. A possible explanation for the disappearance of signal from amorphous Si could be a formation of crystalline Si precipitates. Such phase

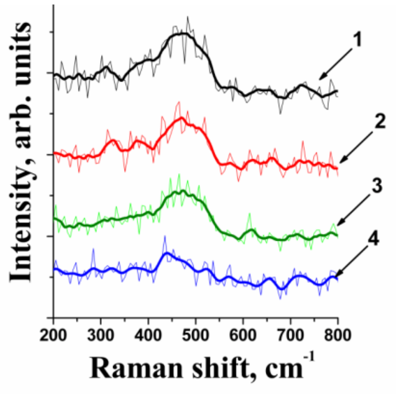

Fig. 3. RS spectra (λ_{exc}=355 nm) of the as-deposited sample and the samples irradiated with swift Xe^+ ions: 1 – as-deposited; 2 – 10^9 cm^{-2}; 3 – 10^{12} cm^{-2}; 4 – $10^{14}cm^{-2}$

transformation should result in an appearance of low-energy tail of the Si-band at 520 cm^{-1} in RS spectra [13]. Though, we did not observe any Si band shape distortion in RS spectra of irradiated and annealed SiN_x/Si samples (not shown). In other words, RS method did not reveal any signs of the formation of nanocrystalline Si phase in the irradiated nitride matrix. The other possible explanation is the dissolution of Si amorphous clusters in nitride matrix during SHI irradiation. More detailed investigation of structural-phase transformation in Si-riched nitride films under SHI irradiation is in progress now.

No luminescence was registered for the as-deposited nitride sample. The PL spectrum of annealed nitride film is shown in Figure 4. A broad band with complicated shape is dominated in a range of 370 – 800 nm. The SHI irradiation results in PL quenching at the fluencies of 10^{12} cm^{-2} and higher.

Conclusion

In summary, we have studied the effects of 200 MeV-Xe^+ irradiation with fluencies (10^9-10^{14}) cm^{-2} on the optical properties and structure of Si-rich SiN_x film deposited on Si substrate by low pressure chemical vapor deposition.

It has concluded that the SHI irradiation results in the dissolution of amorphous Si nanoclusters in nitride matrix. It has been shown, too, that the SHI irradiation leads to quenching a visual PL from nitride films. It can be expected that additional SHI irradiati-

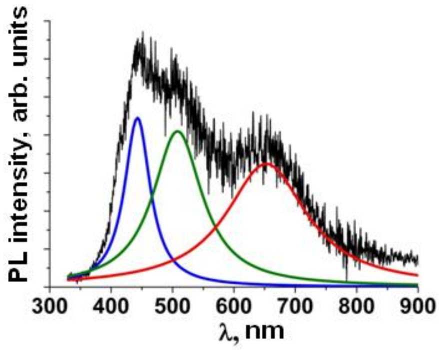

Fig. 4. PL spectrum of the sample after annealing (1100°C, 60 min)

on before annealing can result in the formation of Si phase in nitride matrix with less Si excess in comparison with the ordinary thermal annealing.

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