THE MORPHOLOGY AND OPTICAL PROPERTIES OF Fe, Cr AND Mg SILICIDE NANOCRYSTALLITES BURIED IN SILICON BY ION IMPLANTATION, PULSED TREATMENTS AND Si OVERGROWTH

N. G. GALKIN, K. N. GALKIN, E. A. CHUSOVITIN, S.V. VAVANOVA, A. M. MASLOV, D. L. GOROSHKO, V. O. POLYARNYI

Institute of Automation and Control Processes of FEB RAS, Vladivostok, Russia

R. M. BAYAZITOV, R. I. BATALOV

Kazan Physics-Technical Institute of Kazan Scientific Center of RAS, Kazan, Russia

G. D. IVLEV

Institute of Physics NASB, Minsk, Belarus

The morphology and optical properties of Si samples implanted by Fe, Cr and Mg ions have been studied before and after pulsed annealing by laser and ion beams. Ultrahigh vacuum cleaning and epitaxial growth of Si films with thickness up to 500 nm have been carried out for Si with Fe and Cr silicide nanocrystallites. Optimum conditions of pulsed treatments have been determined for all samples.

1. Introduction

In recent years the considerable attention has been paid to the formation of isolated precipitates of different semiconducting silicides (β-$FeSi_2$, $CrSi_2$, Mg_2Si) in Si due to the possibility of their application in nanoelectronics and optoelectronics as light emitters, IR sensors or thermoelectric materials. The main methods for the formation of β-$FeSi_2$ ($CrSi_2$, Mg_2Si) nanocrystallites (precipitates) are Fe^+ (Cr^+, Mg^+) implantation in Si and reactive deposition epitaxy of Fe (Cr, Mg) monolayers followed by molecular beam epitaxy (MBE) of Si [1]. Pulsed treatments of the implanted layers by nanosecond laser and ion beams are the alternative to the ordinary high-temperature and long-term furnace annealing, which is undesirable for device structures because their parameters essentially degrade due to rapid diffusion of Fe and Cr atoms or re-evaporation of Mg atoms at elevated temperatures. We had earlier demonstrated the formation of β-$FeSi_2$/Si heterostructures by low-energy Fe^+ implantation and pulsed treatments by ion and laser beams [2,3]. Recently we also demonstrated for the fist time the formation of buried β-$FeSi_2$ precipitate layers by Fe ion implantation and Si overgrowth by MBE [4]. However, to the best of our knowledge, pulsed treatments have not been applied yet to Si layers implanted by low-energy Cr^+ and Mg^+ ions.

In this study the low-temperature growth technology including Cr^+ ion implantation, pulsed annealing, ultrahigh vacuum cleaning and Si MBE growth was applied for the first time. The influence of pulsed ion beam treatment (PIBT) on the silicon implanted with different fluencies of low-energy Cr^+ and Mg^+ ions and its optical properties were studied.

2. Experimental

The implantation of Fe^+, Cr^+ and Mg^+ ions into monocrystalline Si wafers with (100) and (111) orientations was carried out at room temperature with ion energy 40 keV and fluencies $F = 6 \cdot 10^{15}$-$6 \cdot 10^{16}$ cm^{-2}. PIBT of the implanted Si layers was carried out using pulsed ion accelerator, which generated high-energy nanosecond carbon ion beams (C^+, $E = 300$ keV, $\tau = 50$ ns). Pulsed energy density varied in the range of $W = 1.0$-1.5 J·cm^{-2} and the fluence of C^+ ions did not exceed 10^{13} cm^{-2}. Besides PIBT we have used pulsed laser annealing (PLA) of the implanted Si layers in air by ruby laser radiation ($\lambda = 0.69$ µm, $\tau = 80$ ns, $W = 1.5$-2.0 J/cm^2).

Si overgrowth was performed in two UHV chambers with a base pressure of $P = 2 \cdot 10^{-10}$ Torr and $P = 1 \cdot 10^{-9}$ Torr. Both chambers were equipped with sublimation Si sources. The first chamber was equipped with an Auger electron spectrometer (AES); the last one had low energy electron diffraction (LEED) facility for *in-situ* study of the structure of the grown Si layers. Low-temperature cleaning (LTC) procedure including heating at 850°C and deposition of Si at a rate of about 0.1 nm/min was used for the creation of atomically clean Si surface for subsequent epitaxial growth. The temperature of Si substrate during Si overgrowth was maintained at 700°C.

The morphology of the implanted Si surface before and after PIBT and PLA was studied by atomic force microscopy (AFM) using Solver P47. The optical spectra of Si samples at different stages were investigated using an automatic spectrophotometer Hitachi U-3010 and an automated monochromator MSDD-1000 at room temperature. Raman spectra were registered at room temperature with the scanning probe multimode microscope NTEGRA SPECTRA (NT MDT, Russia).

3. Results and discussion

The comparative analysis of the changes in the morphology of Si implanted by Fe^+, Cr^+ and Mg^+ ions before and after pulsed treatments was carried out on the base of AFM data. Optical and Raman spectroscopy data for Si samples implanted by different fluencies of ions indicated the amorphous state of the Si surface and segregation of silicides on the surface at large impurity fluencies. The AFM data indicated that the surface is smooth enough with root mean square roughness (σ_{rms}) less than 0.5 nm.

PLA of Fe-implanted samples leads to the development of 3D islands which are probably silicide grains formed at the surface due to Fe segregation [3]. Increasing of PLA energy density results in a minor decrease of the island density due to the diffusion of Fe into Si. It was found that the roughness σ_{rms} of the surface is increased up to several nm with increasing of implantation fluence and pulse energy density. According to Raman spectroscopy the crystallization degree is decreased with increasing of the implantation fluence. This can be related to larger thickness of the implanted (amorphous) layer compared to the melt depth. Therefore, the PLA does not seem an optimal method for efficient recrystallization of Fe-implanted Si and creation of smooth surface for subsequent epitaxial growth.

PIBT of Cr-implanted Si results in full crystallization of the Si layer at fluencies up to $1 \cdot 10^{16}$ cm^{-2}. Precipitates of chromium silicide with semiconductor type of absorption (probably $CrSi_2$) are formed at the depth more than 20 nm by data of optical and Raman spectroscopy. The increase of implantation fluence up to $6 \cdot 10^{16}$ cm^{-2} results in an increase of the precipitate density up to $6 \cdot 10^{9}$ cm^{-2}, increase of roughness (up to 6.9 nm). The subsequent Si growth was non-epitaxial.

By data of optical and Raman spectroscopes (Fig. 1) PIBT of Mg implanted Si ($F \leq 1 \cdot 10^{16}$ cm^{-2}) with low pulse energy density ($W \leq 1$ J/cm^2) results in re-crystallization of Si top layer. decay of magnesium silicide in subsurface region and partial Mg desorption from the surface. An increase of Mg^+ fluence up to $6 \cdot 10^{16}$ cm^{-2} results in a deterioration of the crystal quality of silicon and increase of Mg_2Si precipitate density. PIBT with high pulse energy density ($W \approx 1.5$ J/cm^2) results in a conservation of Mg_2Si on depth down to 30 nm and best crystallization of top silicon layer. This energy density is near optimal for the crystallization of Si, formation Mg_2Si phase and subsequent Si overgrowth.

The investigation of influence of ultra high vacuum LTC both on the surface morphology and epitaxial growth of Si was carried out for Fe- and Cr-implanted samples. The samples subjected to PLA (with Fe^+), PIBT (with Cr^+) and without any treatment were studied by Auger electron spectroscopy and electron energy loss spectroscopy. It was established that thin SiO_2 films is removed from the surface during annealing at 850°C and exposure with silicon at a rate not more than 0.1 nm/min for 20 min. The LTC procedure results in an increase of surface

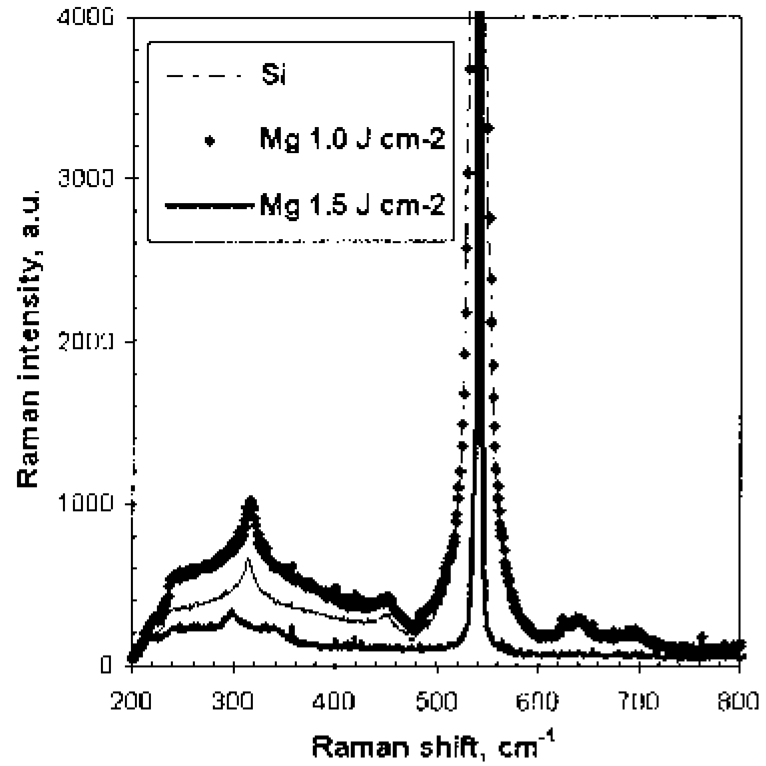

Figure 1. Raman spectra for virgin and Mg-implanted Si ($1\cdot10^{16}$ and $6\cdot10^{16}$ cm^{-2}) annealed with 1.0 and 1.5 $J\cdot cm^{-2}$ pulse energy densities, respectively.

roughness up to 3.0 nm due to formation of 3D silicon and silicide islands. The island sizes are increased with increasing of the implantation fluence.

The investigation of epitaxial Si growth atop atomically-clean Si surface implanted with Fe^+ (Cr^+) ions and subjected to PLA or PIBT was carried out. It was established that epitaxial Si growth by MBE is possible for minimal fluence by mechanism of 2D nucleation and lateral 3D growth. The continuous epitaxial Si films can be obtained larger than 500 nm at 700°C for small implantation fluence of Fe^+ and Cr^- ($\sim10^{16}$ cm^{-2}). For the maximal fluence ($6\cdot10^{16}$ cm^{-2}) the number of pinholes in the Si layer increases sharply and epitaxial growth is failed. In the case of the Si growth (up to 500 nm) on the surface of non-annealed samples the pinhole density increases for 3-4 times and Si layer is polycrystalline only.

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