Ion beam formation of SiGe nanoparticles in Si$_3$N$_4$

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Semiconductor nanoparticles (NPs) are novel materials systems that lie between molecular and solid-state regimes with unique properties largely controlled by their size and shape. Due to their exceptional optical and electrical luminescence, semiconductor NPs may play a key role in the emerging field of nanotechnology with applications in optoelectronic devices. In particular, Ge NPs embedded in a dielectric matrix are of interest because of their ability to emit light$^1$ and store charges$^2$. As a consequence, Ge NPs are promising candidates for novel optoelectronic and non-volatile memory devices.

Previous studies have investigated the structural and vibrational properties of Ge NPs embedded in SiO$_2$.$^3$ Here, we discuss the structural properties of Ge NPs synthesised by ion implantation in amorphous (a)-Si$_3$N$_4$. A uniform ion distribution was achieved through multiple-energy/fluence implantations of Ge ions into 2µm a-Si$_3$N$_4$, which were grown on Si(100) substrates. Implantations were performed at temperatures of -196, 200 and 400 $^\circ$C, to investigate the effect of implanting temperature on the phase of the matrix. In order to promote the growth of NPs, samples were annealed post-implantation at 1100 $^\circ$C for 10 hours in N$_2$ ambient.

Multiple techniques were used to characterise the evolution of the structural properties of samples. The crystalline and amorphous components both as a function of implantation temperature and concentrations, and post-implant annealing were quantified by X-ray Absorption Spectroscopy. The formation of a Si-Ge bonding environments, for all examined concentrations and temperatures was readily evident. For samples implanted at -196 $^\circ$C, second and third nearest neighbor peaks were observed, indicative of crystalline environment. For samples implanted at higher temperatures, however, there was no extended structure indicating that the Ge environment is amorphous for these samples.

Raman spectroscopy measurements were also used to quantify the vibrational properties and composition of each sample and confirmed the implantation-temperature dependent structure. Raman and transmission electron microscopy measurements also show evidence of matrix crystallisation after post-implant annealing for samples implanted at -196 $^\circ$C. In contrast, no evidence of crystallisation was observed for high implanting temperatures. Crystallisation of the nitride matrix enables the rapid diffusion of Ge atoms to the Si/Si$_3$N$_4$ interface. The formation of a thin, non-uniform Ge$_x$Si$_{1-x}$ layer ensued, accompanied by interfacial faceting to relative strain. Here, we discuss the role of implantation and post-implantation conditions on the growth of NPs in a Si$_3$N$_4$ matrix and compare the differences to that previously observed for Ge in SiO$_2$. We find that both implantation and chemical-induced defects appear to be responsible for the various structures that ensue with processing conditions. I have isolated the complex mechanisms responsible for crystallisation of the matrix, including consideration of structure disorders, loss of N$_2$, and non-stoichiometry.