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Raman spectroscopy of porous and bulk GaP subjected to MeV-ion implantation and annealing

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Porous layers on (100)-oriented *n*-type liquid encapsulated Czochralski grown GaP crystals were fabricated by electrochemical etching in a H_2SO_4 aqueous solution and analyzed by scanning electron microscopy. $^{12}C^+$ ions were introduced at room temperature by 3 MeV energy implantation into porous and bulk samples at two ion doses of 10^{14} and $10^{15}\,cm^{-2}$. The prepared samples were annealed in the temperature range between 200 and 600 °C applying rapid thermal annealing (RTA) technique. A comparative micro-Raman study was carried out on the porous and bulk substances. Porosity was found to lead to the violation of the selection rules and to remarkable changes in the optical properties. Additionally, Fröhlich-type modes were observed in the Raman spectra of the porous layers. High energy implantation produces a thin high damaged layer, buried at the depth of the mean projected range. Implantation does not result in a drastic damage of the samples and they undergo a fast recovery after RTA. After this treatment a semi-insulating GaP layer is created, which is thermally stable up to 600 °C. *© 2000 American Institute of Physics.* [S0021-8979(00)02624-4]

I. INTRODUCTION

Stimulated by the observation of the visible luminescence at room temperature from porous silicon,[1] the formation of pores by electrochemical etching emerged as a possibility for controlling the basic properties of semiconductors. Over the last years, beside the study of porous silicon,[2] special interest was paid to porous binary III–V semiconductors. In particular, porous GaP was found to show an enhanced photoresponse, specific scattering properties as well as ultraviolet light emission, while in porous InP a sizable birefringence at a wavelength suitable for optical communication systems was detected.[3–6] Recent reports have displayed a remarkable progress in manufacturing porous III–V structures of different kinds of morphology geometry, of different pore sizes and degrees of porosity.[7–9] Moreover, free standing porous membranes were produced for different schemes of optoelectronic applications.[10]

Nowadays ion implantation is widely used for the purpose of modifying the properties of semiconductors for specific applications. For instance, light ion bombardment at energies higher than 1 MeV with subsequent sample annealing allows one to obtain, e.g., (i) high resistively regions of uniform thickness for inter-device isolation in microwave devices; (ii) confinement layers in heterojunctions; (iii) compensating surface tail states in complex diodes, etc.[11] Additionally, the ion implantation emerged as an important tool for controlling morphology of porous materials and to perform a vertical structuring in the layer volume.[6,10,12]

During implantation, energetic ions encountering a target crystal lose their kinetic energy through two processes: excitation of the electronic system of the solid, and also in nuclear collisions with lattice atoms. The latter process is primarily responsible for displacing substrate atoms from their sites, thereby producing a disorder in solids and creating an expansion of the implanted region.[13] Defects and lattice stress produced by ion implantation can be effectively removed by thermal annealing, at the same time this provides an electrical activation of the implanted impurities.[14,15]

Taking into account possible device applications[16] of porous semiconductor structures, the impact of processing, e.g., ion implantation and rapid thermal annealing (RTA), has to be investigated. Raman spectroscopy represents a powerful technique for obtaining microscopic information about the state of semiconductor material subjected to ion implantation and annealing. There has been considerable interest in applying this technique towards the understanding of the ion implantation and annealing effects in the III–V compound semiconductors,[17–22] since in these materials they can drastically differ from those in Si and Ge.[23,24] In this context the

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