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Diffusion doping of germanium by sputtered antimony sources

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ABSTRACT

Antimony sputter deposition and subsequent diffusion annealing in controlled atmosphere was implemented on Ge wafers, for achieving an optimized n+ doping aimed at the final application of these doped contacts to Ge-based radiation detectors. Two approaches were adopted for n+ doping: diffusion from Sb source sputtered directly on the Ge surface, and diffusion from a remote dopant source. Surface morphology was specifically investigated by electron (SEM-EDS) and atomic (AFM) microscopies. Diffusion profiles were characterized by Secondary Ion Mass Spectrometry (SIMS). The remote doping, obtained by using a Sb-coated Si wafer placed close to the Ge substrate during the diffusion annealing, allowed to attain defect-free surface morphologies and diffusion profiles compatible with well assessed equilibrium diffusion models.

1. Introduction

Small bandgap and high mobility of charge carriers have been recently making germanium (Ge) more and more interesting in several application fields, from photovoltaics to microelectronics, from optics to radiation detectors [1–5]. In the production of Ge-based devices, doping processes used for the realization of n+ and p+ contacts are particularly important and several techniques, such as ion implantation and thermal diffusion [6], are used depending on the final application. For gamma radiation detectors [4], which are based on high purity germanium (HPGe) single crystals, the doped layers in the commercial devices are made by using well-assessed techniques such as boron implantation for p+ contact and lithium evaporation and diffusion for n+ contact. Li-diffused contacts are particularly thick (several hundreds of micron) and are not thermally stable since Li diffusion can continue even at relatively low temperatures (< 400 °C). All these negative features, together with recent advancements in the field of gamma spectroscopy, pushed the development of new alternative techniques for making n+ contacts, in order to achieve more stable and thinner doped layers which can be segmented in the manufacture of high complexity detectors such as AGATA detectors [7].

In this paper, we investigated the realization of n+ contacts on Ge by means of Sb doping. Like for As and P, different techniques can be used to introduce Sb in Ge, such as ion implantation [8–10], vapour phase [11,12], molecular beam epitaxy [13] and organic monolayer-doping [14]. The method described in this paper consists in the sputter deposition of a Sb film and in the following Sb diffusion achieved by thermal treatment. Sb sputter targets are nowadays commercially available with an extremely high purity, which is compliant with the severe requirements of the production process of HPGe detectors. The first approach adopted in this work reckoned on the direct Sb deposition on Ge samples, followed by thermally induced Sb diffusion. The deposited films were characterized before and after thermal treatments using several techniques such as Rutherford Backscattering Spectrometry (RBS), Glancing Angle X-Ray Diffraction (GIXRD), Scanning Electron Microscopy (SEM-EDS), Atomic Force Microscopy (AFM) and Secondary Ion Mass Spectrometry (SIMS). However, this first procedure was discarded owing to the formation of surface defects in the annealed samples. An alternative, successful method was then adopted, consisting in the Sb deposition onto a Si substrate, which was placed close to Ge during the following thermal treatment and used as a Sb remote diffusion source. This method allowed obtaining the Sb diffusion inside the Ge bulk without prejudicing n+ contact continuity.

2. Experimental

2.1. Sample preparation

(100) p-doped ([0.04–0.4 Ωcm] resistivity) Ge wafer (Umicore) was cut into 1 × 1 cm^2 and 1 × 2 cm^2 samples and subsequently cleaned with hot 2-propanol, hot deionized (DI) water and HF 10% to remove dicing adhesive residue and native oxides [16,17]. Besides Ge, silicon

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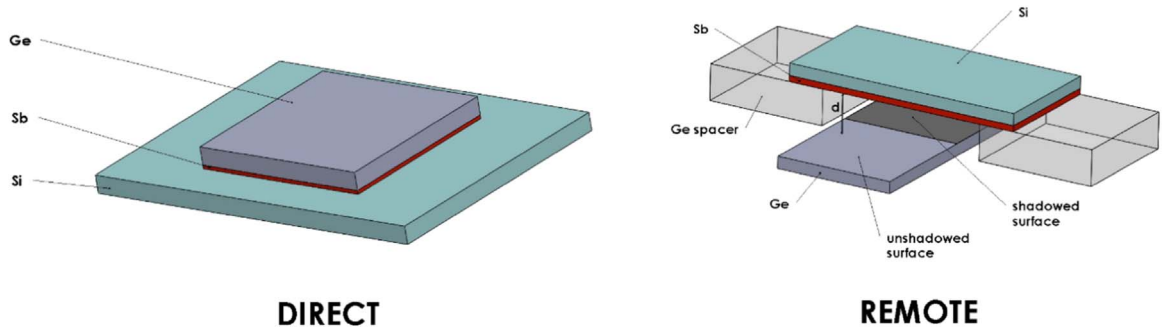

Fig. 1. The two configurations used for Sb diffusion treatments: direct deposition (left); remote deposition (right). In the remote configuration, *d* is the distance between Ge surface and Sb film surface. The Ge surface exactly below the Sb-coated Si was named shadowed surface. The schemes are not in scale.

and glassy carbon substrates were also used for the characterization of different properties of the Sb films and for the remote Sb deposition (silicon, see below). The substrates were put in the sputtering equipment consisting of a stainless steel vacuum chamber evacuated by a turbomolecular pump to a base pressure lower than 1×10^{-4} Pa. The glow discharge sustaining device was a 2-in. cylindrical magnetron sputtering source connected to a radio frequency power generator (600 W, 13.56 MHz), through a matching box. The deposition parameters used for all the films were: direct RF power 30 W; target-to-substrate distance 14 cm; working gas Ar (99.9999% purity); Ar flow 20 sccm. A mass flow controller regulated the working gas flow and the chamber was continuously pumped during the deposition in order to reduce atmosphere contamination by wall outgassing. Pure Sb (99.999%, ACI Alloys) was used as a target. Sb deposition rate, as determined by Rutherford Backscattering Spectrometry (RBS), was 13.3 nm min^{-1} (i.e. 3.76×10^{16} at cm^{-2} min^{-1} with a Sb density of 3.27×10^{22} at cm^{-3}). The duration of each deposition run was varied in order to achieve a film thickness of 20 nm and 100 nm.

Fig. 1 illustrates the two configurations adopted for the Sb diffusion treatments: i) the Sb-coated Ge sample was capped with a piece of Si wafer to limit the Sb sublimation from the film and promote Sb diffusion during high temperature annealing, and the whole was clamped between two quartz slides (direct deposition, left panel in Fig. 1); ii) a Ge substrate was put in the furnace and an Sb-coated Si substrate, used as an Sb source, was placed above two Ge spacers in front of Ge at a fixed distance (remote deposition, right panel in Fig. 1); three different values were chosen for the distance, *d*: 0.2 mm, 1.5 mm and 8.5 mm.

Sb diffusion was performed in a standard tubular furnace equipped with a quartz tube under constant nitrogen flow (about 400 sccm). The latter was established after five vacuum/gas cleaning cycles, aimed at removing contaminants from the furnace. Thermal treatments characterized by quite fast heating ramps (50–170 °C/min depending on the furnace set value) were performed according to the following procedure with fast insertion and extraction of the sample (fast annealing). The furnace was previously heated at a value higher than the desired one (for instance 670 °C to perform a treatment at 610 °C) and then the sample was rapidly inserted, by means of a sample shifter; after a set time had elapsed since the sample insertion and the desired temperature was approached, the sample was rapidly extracted from the tube and left to cool down to room temperature. A thermocouple, recording one temperature value per second, was wired to the sample boat in order to measure the heating ramp. The treatments were carried out at temperatures close to and lower than the Sb melting temperature, i.e. (570 ± 5)°C, (610 ± 5)°C and (630 ± 5)°C. The uncertainty on the temperature value (± 5 °C) is because this is the value reached after a fixed time during fast annealing and depends on many parameters such as starting temperature, sample mass, gas flow, insertion and removal speed, etc. However, we found that this uncertainty was negligible for all the characterizations reported in this work except for the calculation of the diffusion coefficients based on SIMS data. Therefore, hereinafter the true temperature value was used only for SIMS data, while the average value was adopted in all other cases. The heating time, i.e. the time from sample insertion to sample removal, was kept relatively short (30 min) in order to limit the contamination of Ge substrates.

2.2. Characterization techniques

Rutherford Backscattering Spectrometry (RBS) was carried out using 2.0 MeV $^4He^+$ beam at the Van de Graaf accelerator at the Laboratori Nazionali di Legnaro, at the scattering angle of 160°, in order to determine film composition and deposition rate. Samples were characterized by means of glancing angle x-ray diffraction (GIXRD) using a Philips diffractometer equipped with glancing-incidence X-ray optics. The analyses were performed at 0.5° incidence using CuKα Ni filtered radiation at 40 kV and 40 mA. The surface morphology of the samples was investigated both by a SEM (Tescan Vega3 XM) equipped with the energy dispersive spectrometry (EDS) option and by a no-contact-mode AFM modelC-21 (Danish Micro Engineering), mounting a DualScope ProbeScanner 95-50. Secondary Ion Mass Spectrometry (SIMS) was done on diffused samples, by using a Cameca IMS-4f f instrument with an O_2^+ beam, to characterize Sb diffusion profiles. Before the SIMS measurements, the Sb film residue was removed from the surface of the samples by chemical etching.

3. Results and discussion

3.1. Direct Sb deposition

The as-deposited Sb films on both Si and Ge substrates have a very smooth surface as evidenced by SEM images (Fig. 2a). The average roughness, as measured by AFM on a $50 \times 50\ \mu m^2$ area, is low ($R_q < 5$ nm) and is comparable to the substrate one, which is the one typical of a mechanically-chemically polished wafer. RBS analysis of Sb films deposited on glassy carbon substrates confirms their purity, showing that the relative amount of elements incorporated in the film is around 1 at% for Ar and 13 at% for O. Oxygen incorporation is mainly due to the sample staying in the air before the measurements.

The structure of the films deposited on Ge substrates is polycrystalline as evidenced by XRD (Fig. 3, spectrum a): some diffraction peaks typical of the rhombohedral structure of Sb (a = 4.30 Å, c = 11.22 Å) appear in the spectrum of the as-deposited film. The preferred orientation of the nanocrystallites in the film is well evidenced by the lack of the main peak ((012) reflection at 2θ = 28.77°), which appears in the spectrum of the Sb powder [15]. The average crystallite size, as calculated by means of the Scherrer formula applied to the most intense peaks, is around 15 nm.

The effects of heating temperature on the properties of Sb films were studied by different techniques in the range from 570 °C to 630 °C. SEM photos of treated samples (Fig. 2b to d) point out a substantial change of the surface morphology consisting in the appearance of grain-like structures with lateral sizes in the order of micrometres. These