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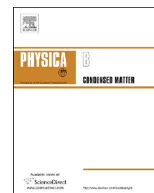

Unexpected properties of the inductively coupled plasma induced defect in germanium

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ABSTRACT

Inductively coupled plasma (ICP) etching of germanium introduces a single defect, the $E_{0.31}$ electron trap, for a large range of argon partial pressures from 4×10^{-3} to 6.5×10^{-4} mbar that correspond to ion energies of 8 to 60 eV. Ge of three crystallographic orientations, (1 0 0), (1 1 0) and (1 1 1), treated with 20 and 60 eV ICP had defect concentration profiles that were similar in appearance, with a maximum concentration of 10^{14} cm^{-3} extending more than a μm into the material, approximately three orders of magnitude deeper than what TRIM simulations predicted. All profiles were measured using Laplace deep level transient spectroscopy (L-DLTS), a technique that is sensitive to defect concentrations as low as 10^{11} cm^{-3}. Isochronal annealing of samples showed concentration curves broadening after a 400 K anneal and decreasing to the 10^{13} cm^{-3} level after a 450 K anneal. Unannealed samples measured after a year exhibited similar decreases in defect concentration without broadening of their profiles. A 550 K anneal lowered the defect concentration to levels below the L-DLTS detection limit. Thereafter additional plasma treatment of the surface failed to reintroduce this defect indicating that the structure required for the formation of $E_{0.31}$ was no longer present in the region under observation.

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1. Introduction

Germanium was the semiconductor used to demonstrate the first transistor and continues to show promise as a suitable candidate to use in ultra-fast devices. It remains the best material for gamma ray detectors and far infrared detectors [1]. Process induced defects are unfortunately introduced during device manufacture; such defects either improve device performance [2] or, as in the case of photo-voltaics, impair their function [3]. Sputter etching is a key technology in the manufacture of semiconductor devices with RF sputter etching and deposition being the most popular in this industry as large wafers can be processed uniformly [4]. With low energy ions producing low ion damage [4,5], high plasma density and the availability of large area sources, inductively coupled plasma (ICP) etching may in future displace capacitively coupled RF plasma sources as the technology of choice to etch large wafers.

Argon ICP etching introduces only one defect in Ge [6], $E_{0.31}$, with an energy level $E_c - 0.31$ eV and an apparent capture cross-section of 3.5×10^{-14} cm^2. This defect has not been observed after MeV electron irradiation [7,8], alpha particle irradiation [9], sputter deposition [10] or electron beam deposition [11] but was observed after dc-hydrogen plasma passivation [12]. Comparing DLTS spectra, the $E_{0.31}$ defect reported on in sputter deposition [10] exhibits a peak at 150 K at a rate window of 80 s^{-1} whereas the ICP induced defect has a peak at 157 K. The Arrhenius plots of these two defects further confirmed that they are different defects. The inertness of argon and the low energy of the ICP Ar ions (measured by the source manufacturer using a Faraday cup) make it unlikely that $E_{0.31}$ would be introduced during high energy processes where conditions are very different. The reproducible introduction of a single defect provides the ideal platform to study the effect of this defect on the properties of a well-known semiconductor. Our focus for this work was to observe the introduction of $E_{0.31}$ in ultra-pure n-type Ge crystals with crystallographic orientations (1 0 0), (1 1 0) and (1 1 1), all bulk grown by Umicore but with differing Sb concentrations of 9×10^{14}, 2.3×10^{14} and 1.3×10^{15} cm^{-3}, respectively. Samples, one of each crystallographic orientation, were processed simultaneously and thereafter Laplace deep level transient spectroscopy (L-DLTS) [13] was used to obtain the defect concentration profiles of $E_{0.31}$ in our samples.

2. Experimental procedure

Electronic grade polished Ge wafers with carbon and oxygen impurity concentrations lower than 10^{16} cm^{-3} (measured using SIMS) of three crystallographic orientations, (1 0 0), (1 1 0) and (1 1 1), were diced into 3 × 5 mm pieces. These were subsequently

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degreased in successive 5 min ultrasonic baths of trichloroethylene, isopropanol and methanol followed by a 1 min etch in 1:5, H_2O_2: H_2O. AuSb (0.6% Sb) was evaporated resistively onto the back surface of all the samples and annealed at 625 K for 10 min in Ar to lower the resistance of these contacts thus making them ohmic. The same wet cleaning procedure was followed prior to loading one sample of each crystallographic orientation into the vacuum chamber for ICP etching using a Copra 160 source from CCR Technology. This source produces an ion energy distribution curve with two narrow peaks with a full width half maximum that is less than 1/3 of the maximum energy. The quoted values herein are for the high energy peaks. The ICP system chamber was pumped down to 1×10^{-6} mbar before being backfilled with Ar up to a partial pressure of 6.5×10^{-4} mbar or 1×10^{-3} mbar for the 3 min or 10 min ICP treatments respectively at 550 W plasma power and 1.5 A coil current. Plasma etching was followed by resistive evaporation (RE) of a 25 nm thick Pd layer through a stainless steel contact mask thus forming eight Schottky barrier diodes 0.6 mm in diameter on the front surface of each sample. RE is known to not introduce defects in quantities measurable by DLTS but diodes prepared by electron beam deposition (EBD) after ICP would also be suitable as no additional defects were observed in such samples.

Current–voltage (*IV*) and capacitance–voltage (*CV*) measurements were performed at room temperature to establish the ideality factor, reverse bias current at 1 V, carrier concentration and built-in voltage V_{bi} of the diodes. Only diodes with an ideality below 1.2 and a reverse bias current below 3×10^{2} A cm^{-2} were considered suitable for further investigation. Applying conventional DLTS confirmed that $E_{0.31}$ was introduced and thereafter L-DLTS was used to determine the peak amplitude at a fixed temperature while varying the filling pulse from 0.1 V to 5 V. In Fig. 1 the DLTS peak amplitudes can be converted to concentration of deep levels, N_T, as $(N_T/N_D)\cong(2\Delta C/C)$ where N_D is the concentration of shallow impurities, ΔC is the DLTS peak height and C is the junction capacitance. To calculate the defect concentrations plotted in Figs. 2–4 the approach of Zohta and Watanabe was used [14].

Samples were isochronally annealed for 10 min at 375 K, 400 K, 450 K, 500 K and 550 K in an Ar ambient and measured (*IV* and *CV*) after each annealing cycle. Long-term study samples were kept at room temperature (RT) between measurements.

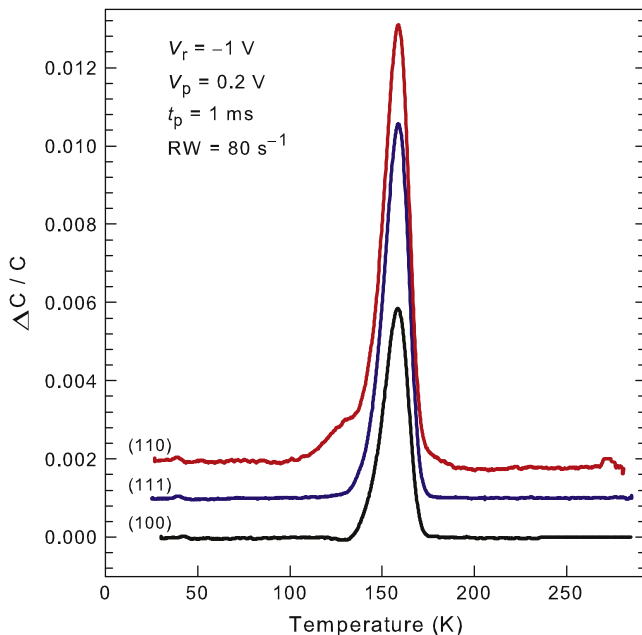

Fig. 1. DLTS spectra of resistively evaporated Pd diodes on ICP etched Ge (1,0,0), (1,1,0) and (1,1,1). The three samples were co-processed and received 3 min of ICP etching. Spectra were recorded at a rate window of 80 s$-^1$, pulse width of 1 ms, quiescent reverse bias of −1 V and a filling pulse with an amplitude of 1.2 V. To distinguish between spectra the (1 1 1) and the (1 1 0) plots have been offset by 0.001 and 0.002 along the *y*-axis, respectively. Some measurements exhibit higher background noise but this did not influence the results.

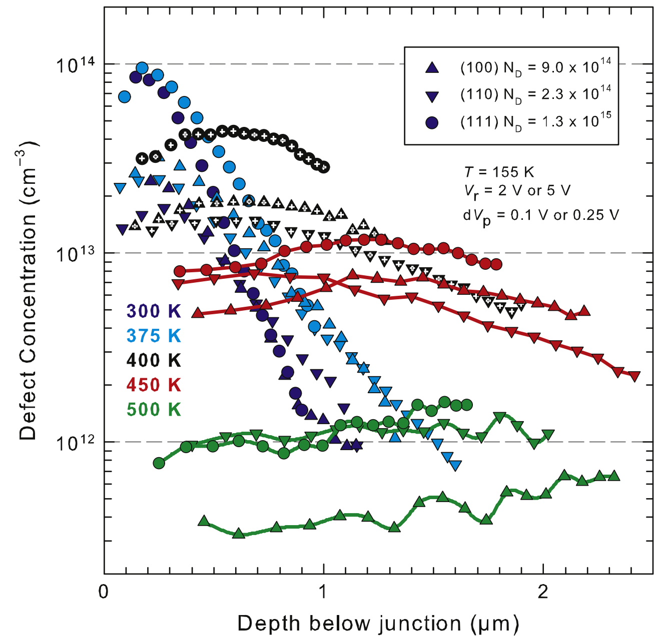

Fig. 2. Depth profiles of the ICP induced $E_{0.31}$ defect in Ge (1,0,0), (1,1,0) and (1,1,1) recorded directly after 3 min ICP etching at an Ar partial pressure of 7×10^{-4} mbar and diode fabrication with subsequent measurements taken after 10 min isochronal annealing at 375 K, 400 K, 450 K and 500 K, respectively. Peak amplitudes for pulses varying from 0.1 V to 2 V or 5 V were determined using L-DLTS.

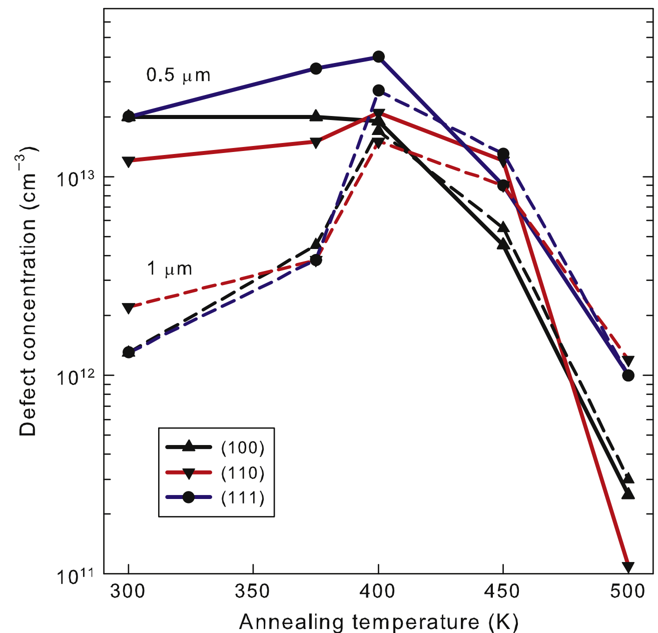

Fig. 3. A summary of Fig. 2, plotting defect concentration versus annealing temperature at 0.5 μm and 1 μm below the metal–semiconductor interface, respectively.

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