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Characterization of As Implanted and Annealed Ge by Photoemission and Electrical Measurements

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1. Introduction

Formation of low-resistnace shallow n^+/p junction is one of key issues to realize better performance Ge n-channel MISFETs. For the case with the n-type dopant activation such as P and As ions, the relatively higher thermal budget is required, while the p-type dopants in Ge can be activated at 400 ºC due to low diffusivity and high activation levels above solid solubility [1, 2]. As for the As^+ ion implantation in Ge at a dose over $4x10^{14}$ cm^{-2}, activated dopant concentrations after the annealing at 500 ºC was saturated at around 10^{18}~10^{19} cm^{-3} [1, 3]. Moreover, no significant decrease in the sheet resistance with increasing dopant concentration was also reported. Based on the study on As implanted Si [4, 5], a formation of small inactive As clusters was considered as a possible cause of these phenomena. An insight into the detailed electronic states of implanted As^+ ions is important to further improvement of activation.

So far, it has been reported that photoemission measurements are the powerful tool to evaluate the surface Fermi level position of semiconductors [6, 7]. In fact, for the case with heavily As implanted Si, chemical bonding features of implanted As atoms such as the As clusters (or interstitial As) and substitutional As have been identified from the binding energy position of core-line signals measured by x-ray photoelectron spectroscopy (XPS) [4,8].

In this paper, we have investigated chemical structures of heavily As^+ ion implanted and annealed Ge (100) and the electrical properties systematically. In addition, the electronic activation of implanted As atoms in Ge(100) was directly evaluated by using an XPS technique.

2. Experimental Procedure

P-type Ge(100) wafers with a resistivity between 18 to 35 Ω·cm were used in this study. After removal of Ge surface oxide by wet-chemical cleaning, As^+ ions were implanted at 10 keV at three different doses of $5x10^{14}$, $1x10^{15}$, and $5x10^{15}$ cm^{-2}. The ion beams were tilted by 7º with respect to the normal to the sample surface. Then, the activation annealing in the temperature range from 400 to 600 ºC was carried out in N_2 ambient for 4min.

3. Results and Discussion

The crystallinity of As implanted Ge at a dose of $1x10^{15}$ cm^{-2} was evaluated by Raman scattering spectroscopy, in which a 441.6 nm line from He-Cd laser light was incident to the sample surface at a glancing angle of approximately 10º in Ar ambient (as shown in Fig. 1). A broad Raman feature around 275 cm^{-1} due to the amorphous Ge (a-Ge) was observed for the sample just after As^+ ion implantation. After 500 ºC annealing, a sharp signal of the TO phonon mode in the crystalline phase (c-Ge : ~300 cm^{-1}), which has almost the same width with a reference spectrum of Ge substrate, was observed. These results indicate that As^+ ion implanted Ge was fully re-crystallized by annealing at temperatures over 500 ºC, which was also confirmed from spectroscopic ellipsometry (SE) analysis.

The sheet resistances measured before and after activation annealing by using the van-der-Pauw method, are summarized in Fig. 2. The sheet resistance lower than 200 Ω/sq was obtained by 600 ºC annealing, but its implantation dose dependence was fairly weak. These results imply that implanted As atoms are not activated effectively or there remain acceptor-like defects in the implanted region. In addition to the sheet resistance

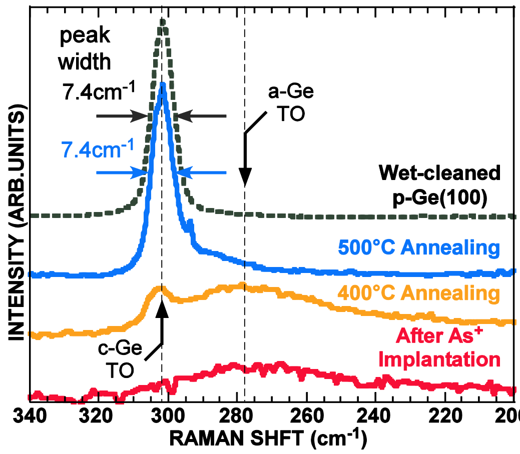

Fig. 1 Raman scattering spectra of As^+ ion implanted Ge at a dose of $1.9x10^{15}$ cm^{-2} before and after activation annealing at 500 ºC for 4min. A spectrum of wet-chemically cleaned Ge(100) substrate was also shown as a reference.

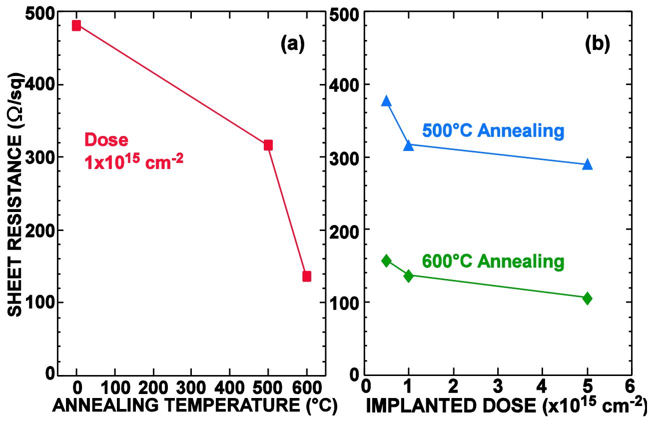

Fig. 2 (a) Activation annealing temperature and (b) implantation dose dependences of the sheet resistance measured by means of the van-der-Pauw method.

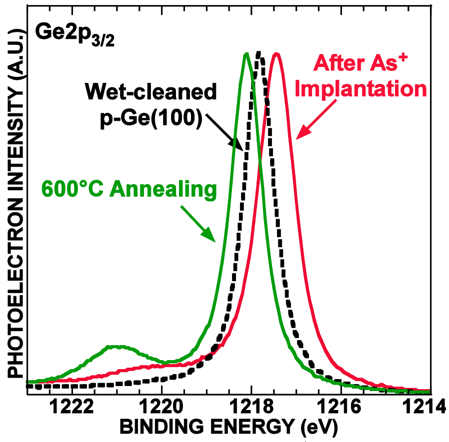

Fig. 3 Ge2p$_{3/2}$ spectra for the As$^+$ ion implanted Ge at a dose of 1.0×10^{15} cm^{-2} before and after 600 ºC annealing for 4min. A spectrum of wet-chemically cleaned Ge(100) was also shown as a reference. The photoelectron take-off angle was set at 30°.

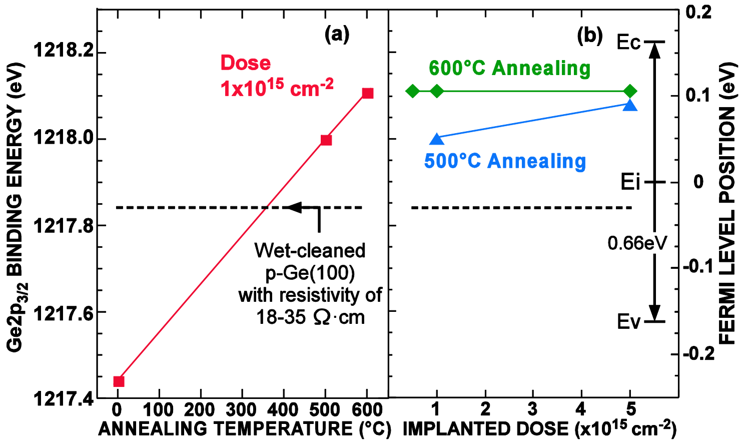

Fig. 4 Changes in the binding energy position of Ge2p$_{3/2}$ signals originating from As$^+$ ion implanted Ge respected to the Fermi energy position with (a) activation annealing temperatures and with (b) implantation dose for the samples after annealing at 500 and 600 ºC.

measurements, the Fermi level positions of doped Ge were evaluated from hard x-ray photoemission spectroscopy (HAXPES) analysis using a synchrotron radiation (hν = 7939 eV). Figures 3 and 4 show the typical Ge2p$_{3/2}$ spectra measured at each step in the sample fabrication and the observed energy position of Ge2p signals originating from As$^+$ ion implanted Ge layer, respectively. By As$^+$ ion implantation at a dose of 1x10^{15} cm^{-2} (as shown in Fig. 3), Ge2p$_{3/2}$ signals were shifted toward a lower binding energy (B.E.) side as compared to the reference spectrum of wet-chemically cleaned p-type Ge(100). The observed energy shift is attributable mainly to the generation of acceptor-like defects and partly to an increase in the Ge energy bandgap due to the amorphization by ion implantation. Also, observed energy shift of Ge2p$_{3/2}$ signals toward the higher B.E. side by the annealing indicates that the Fermi level moves toward the conduction band as a result of the electrical activation of implanted As dopants. In addition, no significant difference in Fermi level position between the samples after annealing at 500 and 600 ºC with different implanted dose was observed (Fig. 4 (b)), being consistent with the results of Fig. 2 (b).

To get a better understanding of the As activation in Ge, chemical bonding features of As atoms for the samples with different implantation dose after 600 ºC annealing were investigated from As2p$_{3/2}$ spectra as shown in Fig. 5. Note that, a change of As2p$_{3/2}$ signals in lower binding energy region with implantation doses was observed clearly (Fig. 5(a)). Considering the difference in electronegativity between Ge and As, measured As2p$_{3/2}$ spectrum was deconvoluted into two components originating from activated As (As^{1+}) and inactivated As (As^{0+}) including As cluster as shown in Fig. 5(b). From the signal intensity ratio of As^{1+} component to the total (As^{1+}/(As^{0+}+As^{1+})), the As activation ratio was estimated to be 12% for the case with a dose of 5x10^{14} and 8% for the case with 5x10^{15} cm^{-2}.

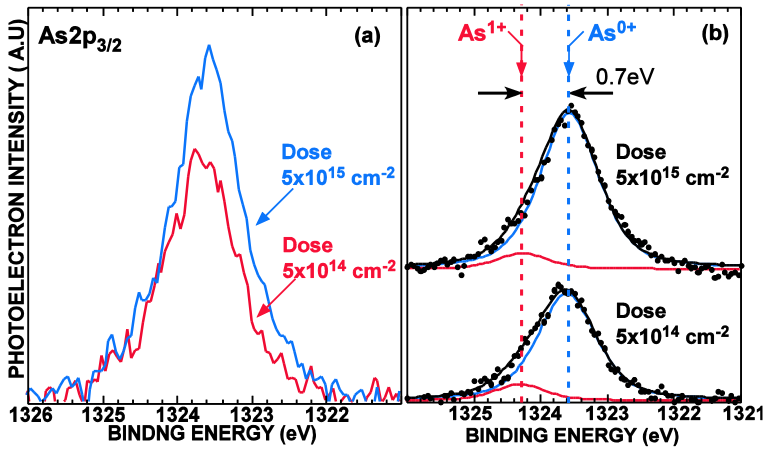

Fig. 5 (a) Measured and (b) deconvolued As2p$_{3/2}$ spectra taken for the samples with different implantation doses after activation annealing at 600 ºC. The photoelectron take-off angle was set at 30°.

In summary, XPS analyses of heavily As implanted Ge after annealing show the presence of two chemical states due to activated substitutional As and inactivated As clusters. The result suggests that the suppression of As cluster formation is important to improve the As activation.

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