дозы имплантированных ионов ксенона, используемых в качестве маркера. Концентрация в максимуме профиля смещенных из узлов атомов кремния, полученная при имплантации ионов ксенона, уменьшается в процессе ионно-ассистированного осаждения титановых и кобальтовых покрытий. При этом проявляется тенденция снижения слоевой концентрации радиационных дефектов. Предполагается, что наблюдаемые явления связаны с активацией процессов проникновения компонентов покрытия в глубь кремния, а также процессов миграции дефектов на большие глубины и в покрытия под воздействием облучения формируемых структур ассистирующими ионами. Установлено, что в процессе ионно-ассистированного нанесения тонких пленок титана и кобальта в их состав входят, кроме атомов осаждаемого металла, атомы углерода, кислорода и водорода, а также атомы подложки.


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# MECHANISM OF HYDROGEN-RELATED SHALLOW DONORS FORMATION IN $Ge_{1-x}Si_x$ CRYSTALS IMPLANTED WITH PROTONS


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It is found that shallow hydrogen-related donors are formed in the proton-implanted dilute $Ge_{1-x}Si_x$ alloys ($0 < x < 0.031$) as well as in Si-free Ge samples upon heat-treatments in the temperature range 225 - 300 °C. The maximum concentration of the donors is about $1.5\cdot10^{16}$ cm$^{-3}$ for a $H^+$ implantation dose of $1\cdot10^{15}$ cm$^{-2}$. Formation and annihilation temperatures of the proton-implantation-induced donors do not depend on the Si concentration in $Ge_{1-x}Si_x$ samples. However, the increase in Si content has resulted in a decrease of the concentration of the H-related donors. The possible origin of the H-related donors and mechanisms of Si-induced suppression of their formation are discussed.


## 1. INTRODUCTION

Hydrogen is a ubiquitous impurity in semiconductors. It is introduced inadvertently during plasma processing, wet etching, polishing and some cleaning processes [1, 2].

Previously [3] we found that heat-treatments of the proton-implanted Ge samples in the temperature range 200-300 °C result in the formation of shallow hydrogen-related donors. The maximum concentration of the donors is about $2\cdot10^{16}$ cm$^{-3}$ for a $H^+$ implantation dose of $1\cdot10^{15}$ cm$^{-2}$. An analysis of changes in the spatial distribution of the H-related donors upon isothermal and isochronal anneals has shown that the donors appear in a region which is close to the projected depth of implanted protons at the initial stages of heat-treatments in the temperature range 200 – 300 °C and spread out of this region upon an increase in annealing time or annealing temperature.

Results of a study of defects induced by proton implantations followed by anneals in Ge-rich SiGe alloys are reported in this paper.

## 2. EXPERIMENTAL DETAILS

Samples for this study were prepared from dilute $Ge_{1-x}Si_x$ ($0 < x < 0.031$) alloy crystals, which were grown by the Czochralski technique. The crystals were doped with phosphorus during growth. The phosphorus concentration was in the range $1{\cdot}10^{15}$ to $3{\cdot}10^{15}\ cm^{-3}$. Schottky diodes for capacitance measurements were fabricated by thermal evaporation of Au on polished surfaces. The thickness of deposited Au layers was about 200 nm. The samples were implanted with 300 keV protons ($H^+$) through the Au layers at room temperature. The fluence of implantation was $1{\cdot}10^{15}\ sm^{-2}$. The mean projected depth of 300 keV $H^+$ ions in germanium was calculated to be about 3 μm. 20 minute isochronal annealing of the samples was carried out in the temperature range 50 – 300 °C in a dry nitrogen ambient.

The concentration profiles of shallow donors in the implanted and annealed samples were measured with the use of capacitance-voltage (*C-V*) technique at room temperature. Deep electronic levels were characterized with conventional deep level transient spectroscopy (DLTS).

## 3. EXPERIMENTAL RESULTS

Figure 1 shows changes in depth profiles of uncompensated shallow donors upon isochronal anneals of proton-implanted $Ge_{1-x}Si_x$ samples with different Si content. The donor profiles for as-grown non-irradiated samples are also shown. The proton implantation has resulted in a non-uniform decrease in the concentration of shallow donors in near-surface regions of the samples. The positions of the minima in the donor concentration profiles correspond to the projected depth of implanted protons. According to a combined analysis of the donor concentration profiles and concentrations of deep level defects deduced from DLTS spectra, the decrease in the donor concentration is related to the removal of the donor activity of phosphorus atoms. Isochronal anneals of the implanted samples in the temperature range 50 – 200 °C have not induced essential changes in the donor concentration profiles in all the implanted samples. However, the concentration profiles have been changed drastically upon further anneals at 250 and 275 °C. Anneals at these temperatures have resulted in the substantial increase in the donor concentration in all the samples. The peaks in the donor concentration profiles occur at the projected depth of implanted pro-

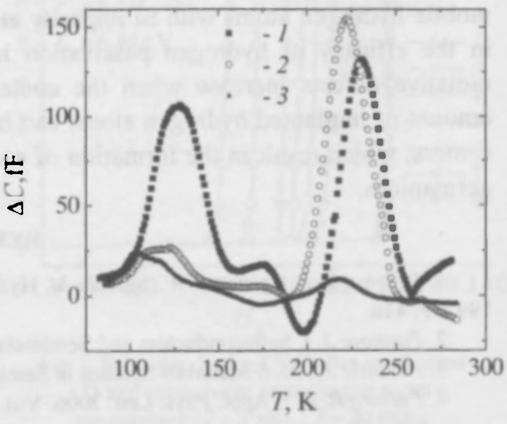


*Fig 1.* DLTS spectra in $Ge_{1-x}Si_x$. *X*, %: *1* – 3.1, *2* – 1.2, *3* – 0.08. Electron emission 2000 $s^{-1}$

tons. Figure 1 shows that the concentrations of the introduced donors significantly exceed the concentrations of shallow donor impurity atoms, which were introduced during growth. It can be seen that the concentrations of donors induced by the proton implantation and the subsequent heat-treatment depend on the silicon content in the $Ge_{1-x}Si_x$ samples. The maximum donor concentration of about $1.5 \cdot 10^{16}$ $cm^{-3}$ has been observed in the crystals with the lowest Si content (0.08 at. %). The increase in the concentration of silicon atoms in the GeSi alloy samples results in a decrease in the concentration of the proton-implantation-induced donors. In a GeSi crystal containing 3.1 at. % Si atoms the maximum donor concentration is about $5 \cdot 10^{15}$ $cm^{-3}$.

## 4. DISCUSSION AND SUMMARY

The introduction of shallow donor centers into Si crystals as a result of proton implantation followed by annealing in the temperature range 300 – 400 °C is a well-documented fact [1, 2]. It was suggested that these donors are related to complexes of hydrogen atoms with intrinsic interstitial-related defects induced by the implantation, however the microscopic structure of the proton-implantation-induced donors is still not well understood.

The results of the present study show that shallow donor centers are introduced also in dilute $Ge_{1-x}Si_x$ alloy crystals subjected to a proton implantation followed by heat-treatments in the temperature range 225 – 275 °C. It appears that the formation and annihilation temperatures of the proton-implantation-induced donors do not depend on the Si concentration in the $Ge_{1-x}Si_x$ samples. However, the increase in the Si content has resulted in a decrease in the concentration of the H-related donors (Fig. 1). According to results of a recent infrared absorption study [4], Si impurity atoms in Ge-rich SiGe alloys can serve as effective traps for mobile hydrogen atoms and some of the observed Si-H complexes are found to be stable up to 200 °C. Taking into account these findings, it can be suggested that the observed decrease in the concentration of proton-implantation-induced shallow donors with the increase in the Si content in the $Ge_{1-x}Si_x$ samples is related to interactions of mobile hydrogen atoms with Si impurity atoms. On the other hand it leads to the decrease in the efficacy of hydrogen passivation in consequence of which the concentration of radiative defects increase when the content of Si in allow increases. Thus, a reduced amount of implanted hydrogen atoms can be involved in defect reactions with intrinsic Ge centers, which result in the formation of complexes exhibiting shallow donor properties in germanium.

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