Porosity in Ge and $Si_{1-x}Ge_x$ Alloys Induced by Ion Implantation

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Volumetric swelling and nanoporosity were observed in crystalline germanium (c-Ge) and silicon germanium alloys (c- $Si_{1-x}Ge_x$) irradiated with 140 keV Ge^+ at room temperature (RT) under a range of stoichiometries. Multi characterization techniques were applied to characterize the surface morphology, including scanning electron microscopy (SEM) transmission electron microscopy (TEM), and optical profilometry. Porosity depends strongly on the ion fluences and Ge stoichiometry. Porosity was observed at x ≥ 0.77 Ge, and shifted to higher fluence as x decreased, compared to pure Ge. The proposed mechanism for pore formation in the alloys is vacancy segregation and clustering combined with preferential sputtering at the surface.

1. Introduction

Even though porosity must be avoided in most electronic applications, it is highly required in a wide range of applications such as solar cells[1], filters[2], gas sensors[3] as well as anodes for electric batteries[4]. In the last three decades, there has been renewed interest in porosity particularly in Ge because of its interesting properties including smaller band gap and high carrier mobility compared to Si[5]. Under certain conditions, ion implantation often leads to drastic evolution in the surface morphology associated with the formation of amorphous porous layers with a thickness of roughly six times higher than the projected ion range[6] as a result of nuclear energy deposition[7]. This structure has been observed under irradiation with a range of heavy ions (e.g Ga^+, In^+, As^+, Sb^+, Bi^+, Mn^+, Sn^+, I^+, Au^+, or Ge^+)[8-13], but does not occur for light ions such as He^+, F^+, BF_2^+, or Al^+[8, 14, 15].

Pore formation in Ge also depends on the substrate temperature. Recently, Stritzker and co-workers[16] revealed the temperature dependence of pore formation. They observed that the formation of a porous structure started from -80 °C to 200 °C, where vacancies are highly mobile and cluster to form voids. Outside of this range, no porous structure was observed. At low temperatures below -80 °C the matrix exhibited an amorphous phase but no pore formation. At > 200 °C Frenkel pairs are highly mobile and supress the formation of amorphous and porous structures. The Porous structure is found to be stable when subjected at thermal annealing. However, porosity is not often observed in Si. The only studied observation of pore formation in Si was by Perez-Bergquist et al.[17] at very high ion flux and temperature: it is unclear what the exact mechanism is in this case. Porosity is not only observed in Ge, but is also pronounced in semiconductor compounds such as GaSb, and InSb[17-18]. Also, a porous structure has been observed in $Si_{1-x}Ge_x$ alloys which will be discussed in detail below. Up to now, there was only one study which observed porosity in the alloys. Romano et al.[12] reported the porous structure was only observed in x=0.9 of Ge content and the structure was in micro size which is larger than the one observed in Ge. On the other hand, this study observed porous structure which is comparable with Ge. There have been two mechanism have been proposed for pore formation, vacancy clustering and so-called “microexplosion”. In the present work our data strongly suggested the vacancy clustering mechanism which governed the formation of porous structure. Here we present new findings on porosity in $Si_{1-x}Ge_x$ alloys with different stoichiometry and compare it with Ge under RT irradiation.

2. Sample preparation

$Si_{1-x}Ge_x$ alloys were prepared by molecular beam epitaxy (MBE) with different content of Ge (x=1.00, 0.83, 0.77, 0.65, and 0.43) and implanted with 140 keV Ge^+ ions under a wide range of fluence from $1x10^{13}$ to $1x10^{18}$ ions/cm^2 at RT. The mean ion flux was ~$1.2x10^{13}$ ions/cm^2/s. To avoid channelling effect the sample holder was misoriented by 7°. Part of the sample was masked to prevent irradiation in this area in order to perform step height measurements. Plain-view scanning electron microscopy (PVSEM) was performed to investigate the sample surface morphology. The structure beneath the surface was observed using cross-section transmission electron microscopy (XTEM).

3. Results

Fig. 1(a-h) shows the plain-view (PVSEM) and cross-section (XTEM) images of the near surface morphology for Ge and $Si_{1-x}Ge_x$ alloys implanted with 140 keV Ge^+ ions at RT for one selected fluence of $2x10^{17}$ ions/cm^2. Generally, the alloys exhibit porosity that is similar to Ge except that the onset of porosity is requires a higher fluence with increasing Si content. The fact that it is more difficult to initiate porosity in alloys is consistent with the fact that it is impossible to generate porosity in a-Si below 300 °C. Furthermore, there is reduction in pore size with reducing Ge content until porosity disappears at $Si_{0.35}Ge_{0.65}$ (see Fig. 1(a-d)). As a result of the absence of a porous structure in $Si_{0.35}Ge_{0.65}$, it can be estimated that the threshold Ge concentration for pore formation should be > 0.65 Ge. The shape of pores is irregular and they are not aligned pore to each other, which is in agreement with other reports [12,19]. The average pore radius was calculated as a function of ion fluence in several SEM micrographs in Fig. 2. Typically more than 1000 pores for each sample were measured indicating that the large standard deviation is not a result of statistical error but reflects the actual pore size variation in each sample. The mean pore radius increases with increasing ion fluence. It is noticeable that pore size for Ge is slightly larger at a given fluence and saturated for Ge and $Si_{0.17}Ge_{0.83}$ at fluence of $5x10^{16}$ ions/cm^2 at approximately 14 nm. The pore radius is reduced for 0.77 Ge and no saturation in pore size was observed. As it can be seen in Fig.1 (e-h), that the thickness of the porous layer is reduced with increasing Si content in the matrix until it vanishes in the $Si_{0.35}Ge_{0.65}$ alloy in good agreement with SEM images. The porous layer consists of a columnar structure (overlying an amorphous phase) separated by thin walls of ~10 nm. The thickness of the porous layer is plotted in Fig. 3 as a function of ion fluence. All the samples showed an increase in thickness with increasing fluence. The pore depth at a fluence of $2x10^{17}$ ions/cm^2 in Ge is about a factor of eight (512 nm) times the projected range (62 nm) calculated by SRIM[20]. The thickness of porous layer in $Si_{0.17}Ge_{0.83}$(241 nm) is about a factor of four the projected range (68 nm), and $Si_{0.23}Ge_{0.77}$ is almost equal to the projected range (72 nm). Although the porous layer thickness for Ge saturated at $5x10^{16}$ions/cm^2, no saturation was observed for the alloys. There is evidence at low fluence from TEM images (not shown) that porosity nucleated at the surface and then developed with continued irradiation. A likely reason for the reduction in pore layer thickness in the alloys compared to Ge is the presence of Si atoms in the matrix which makes it more difficult to generate vacancy clusters and then form voids.

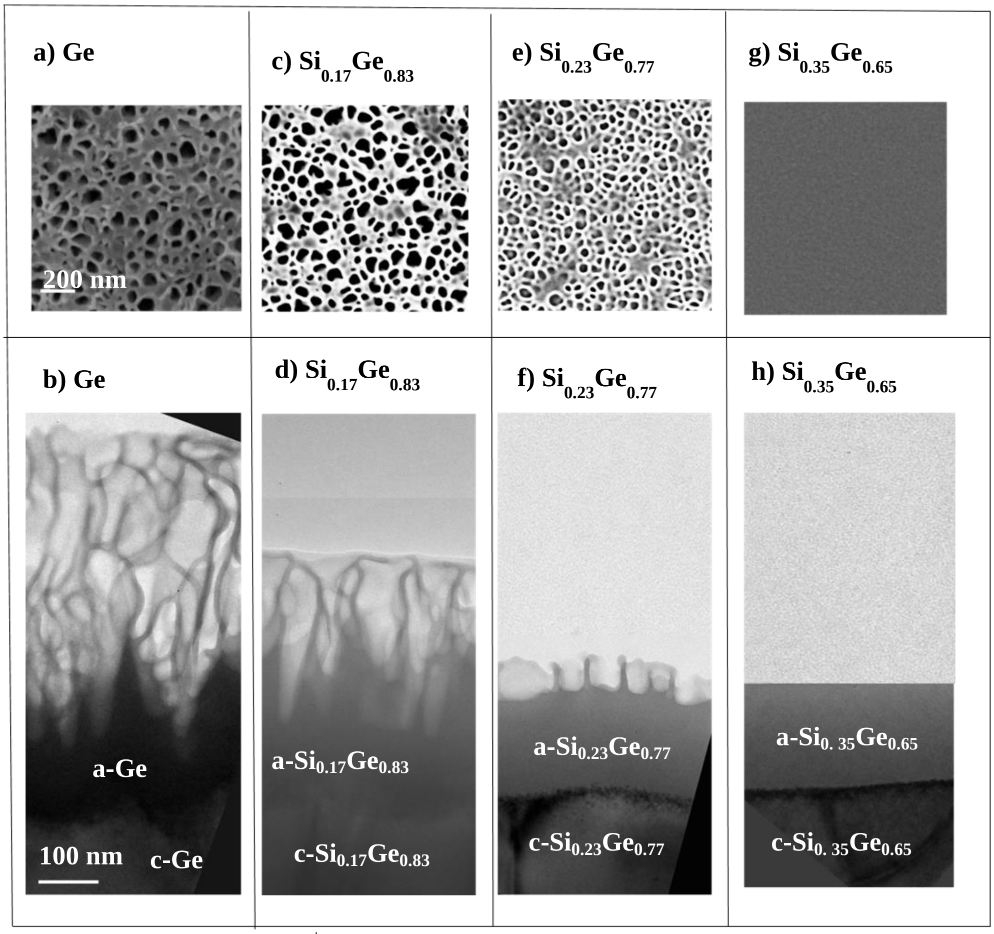

Fig. 1. PVSEM and XTEM images of Ge^+ implanted $Si_{1-x}Ge_x$ alloys with different Ge stoichiometry for the same fluence of $2x10^{17}$ ions/cm^2 (a) (b) in Ge, (c) (d) in $Si_{0.17}Ge_{0.83}$, (e) (f) in $Si_{0.23}Ge_{0.77}$, (g) (h) in $Si_{0.35}Ge_{0.65}$. The scale bar is the same for all PVSEM and XTEM images, respectively.

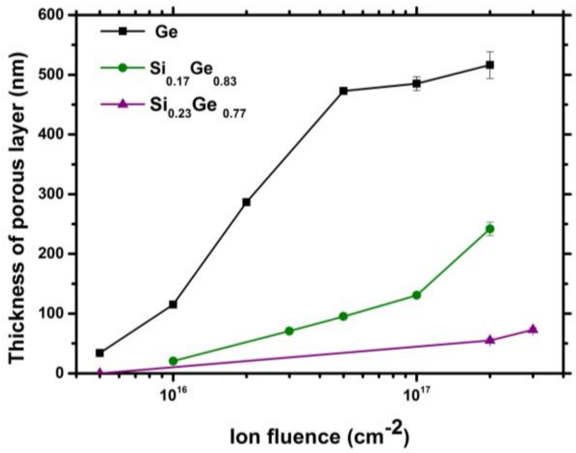

Fig. 2. The pore mean radius as a function of ion fluence for Ge, $Si_{0.17}Ge_{0.83}$, and $Si_{0.23}Ge_{0.77}$.

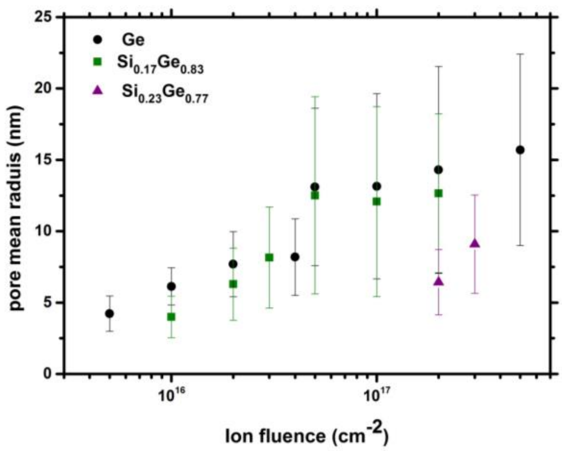

Fig. 3. the thickness of porous layer as a function of ion fluence for Ge, $Si_{0.17}Ge_{0.83}$, and $Si_{0.23}Ge_{0.77}$.

Swelling of the matrix was observed as a direct result of porosity: the swelling increased with increasing fluence as shown in Fig. 4. The onset of pore formation in Ge is at $5x10^{15}$ ions/cm^2, and is shifted to higher fluence for the alloys. The threshold fluence for pore formation is estimated to be $8x10^{15}$ and $1x10^{17}$ for $Si_{0.17}Ge_{0.83}$ and $Si_{0.23}Ge_{0.77}$ alloys respectively. Three distinct regimes are apparent for Ge: stage I shows little swelling (< 3 nm) to a fluence of $2x10^{15}$ as expected by the density reduction during amorphisation [21]. Stage IIL: step increase in the swelling up to 100 nm at a fluence of $2x10^{16}$ ions/cm^2. Stage III: saturation of swelling at $5x10^{16}$ ions/cm^2 up to 178 nm. In the alloys, there are two stages. No swelling in stage I, and then a steep increase in the step height, with no saturation was observed up to the maximum fluence. The alloys exhibited reduced swelling when the matrix contained Si. The data in the current work is much more consistent with a vacancy clustering mechanism that initiates at the surface, and then the pores grow in depth through the amorphous layer, giving rise to swelling. Finally, if the fluence is high enough, it will result in a complex pore structure with saturation in the swelling (see Fig.1 (e)).

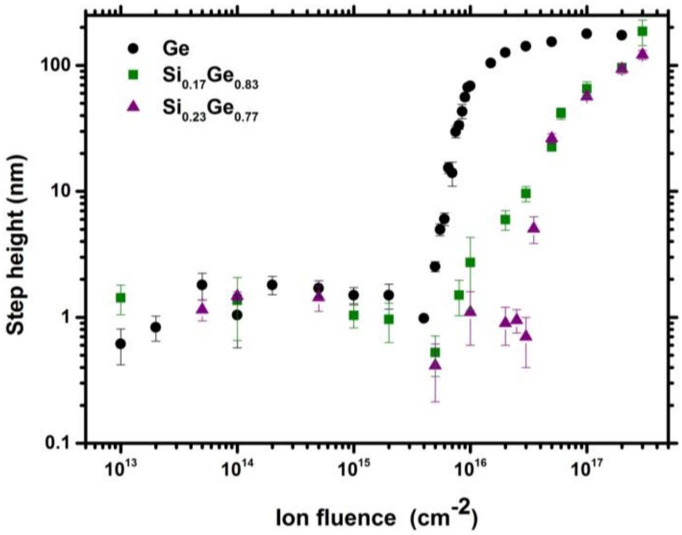

Fig. 4. Volumetric swelling as a function of ion fluence for $Si_{1-x}Ge_x$ alloys with different Ge content at 23°C irradiation.

4. Conclusion

Under the bombarding conditions used, porosity is observed in Ge and $Si_{1-x}Ge_x$ alloys beyond 77% Ge. The formation of a porous structure is shifted to high fluence with increasing Si content. Moreover, we found that the initiation of porosity started at the surface during the onset stage of porosity. We suggest that preferential sputtering of the alloys may play an important role for pore formation.

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References

[1] Sun D, Riley A E, Cadby A J, Richman E K, Korlann S D and Tolbert S H 2006 *Nature* **441** 1126
[2] Föll H, Carstensen J and Frey S 2006 *J.Nanomater.* **2006** 1
[3] Kaltsas G, Nassiopoulos A and Nassiopoulou A G 2002 *Sens.J, IEEE* **2** 463
[4] Rudawski N G, Darby B L, Yates B R, Jones K S, Elliman R G, and Volinsky A A 2012 *Appl. Phys. Lett.* **100** 083111
[5] Bischoff L, Pilz W, and Schmidt B 2011 *J. Appl. Phys.* **104** 1153
[6] Wilson I H 1982 *J.Appl. Phys.* **53** 1698
[7] Romano L, Impellizzeri G and Grimaldi M G 2013 *Mater. Lett.* **96** 74

[8] Appleton B R, Holland O W, Poker D B, Narayan J, and Fathy D 1985 *Nucl. Instrum. Methods Phys. Res., Sect. B* **7-8** 639
[9] Chen Y J 1997 *J. Vac. Sci. Technol. B* **15** 809
[10] Darby B L, Yates B R, Rudawski N G, Jones K S, and Kontos A 2011 *Nucl. Instrum. Methods Phys. Res., Sect. B* **269** 20
[11] Holland O W, Appleton B R and Narayan J 1983 *J. Appl. Phys.* **54** 2295
[12] Romano L, Impellizzeri G, Bosco L, Ruffino F, Miritello M and Grimaldi M G 2012 *J. Appl. Phys.* **111** 5
[13] Wang L M and Birtcher R C 1989 *Appl. Phys. Lett.* **55** 2494
[14] Kaiser R J, Koffel S, Pichler P, Bauer A J, Amon B, Claverie A *et al.* 2010 *Thin Solid Films.* **518** 2323
[15] Darby B L, Yates B R, Rudawski N G, Jones K S, Kontos A and Elliman R G 2011 *Thin Solid Films.* **519** 5962
[16] Stritzker B, Elliman R G and Zou J 2001 *Nucl. Instrum. Methods Phys. Res., Sect. B.* **175** 193
[17] Perez-Bergquist A, Xiang X, Zhang Y and Wang L 2009 *Microsc. Microanal.* **15** 142
[18] Nitta N, Taniwaki M, Hayashi Y and Yoshiie T 2002 *J. Appl. Phys.* **92** 1799
[19] Rudawski N G and Jones K S 2013 *J. Mater. Res.* **28** 1633
[20] Ziegler J F, Biersack J P and Littmark U 1984 *The Stopping and Range of Ions in Solids Vol. 1* (New York : Pergamon)
[21] Roorda S, Sinke W, Poate J, Jacobson D, Dierker S, Dennis *B et al.* 1991 *Phys. Rev. B: Condens. Matter.* **44** 3702