Effect of impurities on the nanostructure formation on Ge (100) substrate by 26 keV ion implantation

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Abstract— In this study a comparison of the 26 keV Si^{-} and Au^{-} ion implantation on Ge (100) substrate at room temperature for the ion fluence of $1\times10^{18}\ ions/cm^{2}$. The study demonstrates that the implantation of Si ions at near normal incidence results in the formation of pit structures on the Ge substrate, whereas the implantation of Au ions produces dot structures. Au ion bombardment can produce a grating-like rippled surface that is highly ordered at an off-normal angle of 60°; however, Si^{-} ions do not exhibit any such ordered ripples. Au ion bombardment can generate beautiful highly ordered grating-like rippled surface but no such ordered ripples are found for Si^{-} ions. A subsequent investigation was conducted by incorporating silver atoms into the Si^{-} ion bombardment of the Ge substrate. The nanostructuring process is improved by the introduction of Ag atoms during the Si^{-} ion bombardment of the Ge substrate.

***Index Terms*—Si ion implantation, Au ion implantation, Ag-assisted Nanostructuring, Ripple structures, pit formation.**

I. INTRODUCTION

Surface engineering is a multidisciplinary field of research that aims to customize the electronic, optical, and magnetic properties of a surface. The nanostructuring of solid substrates is a significant component of surface engineering. A variety of physical [1] and chemical [2] methods are employed to synthesize these nanostructures. The bottom-up approach is in large part dependent on the spontaneous self-organization of nanostructures by energetic ion beams under varying geometrical conditions [3]. In the past four decades, researchers have investigated the formation of self-organized nanostructures using energies ranging from a few electron volts (eV) to hundreds of MeV [4-7]. Low energy ion beams are employed to customize the surface properties, while high energy ion beams are primarily employed for ion implantation and modification [3]. The surface architechuring is significantly influenced by both implantation and sputtering at a few keV energy, crystalline substrate maintains its crystallinity at ultra-low energy ion beams if substrate temperature is elevated but surface modification is mainly surface restructuring. Despite the fact that the first transistor was fabricated on a Ge substrate, Si garnered significant focus in the semiconductor industry for a variety of reasons. Ge has recently garnered the attention of researchers due to its increased electron mobility, narrow band gap, high solubility of dopants, and larger effective excitonic Bohr radius [8]. Bradley and Cuerno's groups have extensively explored the fundamental theories of nanostructure formation [9-11]. The Cuerno group developed the fundamental linear equation of motion, which is based on the sputtering theory and involves the erosion and diffusion of atoms [12]. A subsequent theory was devised that posits that the presence of two atomic species in a solid can result in an unusually high degree of order. Mollick et al. demonstrated that the fabrication of highly ordered nanostructures can be facilitated by heavy metal ions, such as gold ions [13]. Many groups have investigated the impact of impurities on the formation of nanostructures [14-15]. I conducted a comparison of the 26 keV Si^{-} and Au^{-} ion implantation on Ge (100) substrate at ambient temperature for an ion fluence of $1\times10^{18}\ ions/cm^{2}$ in this work. The implanted atoms of Si or Au in the Ge substrate function as impurities, contributing to the evolution of the nanostructured surface, despite the fact that the Ge substrate is a monoatomic substrate. This study demonstrates that the implantation of Si ions at near normal incidence results in the formation of pit structures on the Ge substrate, whereas the implantation of Au ions produces dot structures. In this investigation, I have adjusted the incidence angle from normal to an off-normal angle of 60° in relation to the surface normal. Au ion bombardment can produce a grating-like rippled surface that is highly ordered at an off-normal angle of 60°; however, Si^{-} ions do not exhibit any such ordered ripples. Au, as a heavy metal atom, may be instrumental in the formation of nanostructures. To comprehend the function of metal ions during the surface treatment, Ag atoms were introduced during Si^{-} ion implantation. The nanostructure formation on the Ge substrate is once again influenced by the presence of Ag atoms during Si^{-} ion bombardment. In the field of sensors, detectors, photovoltaic and ultra-fast optoelectronic devices, these nanostructured surfaces offer potential applications [16-17].

II. EXPERIMENTAL

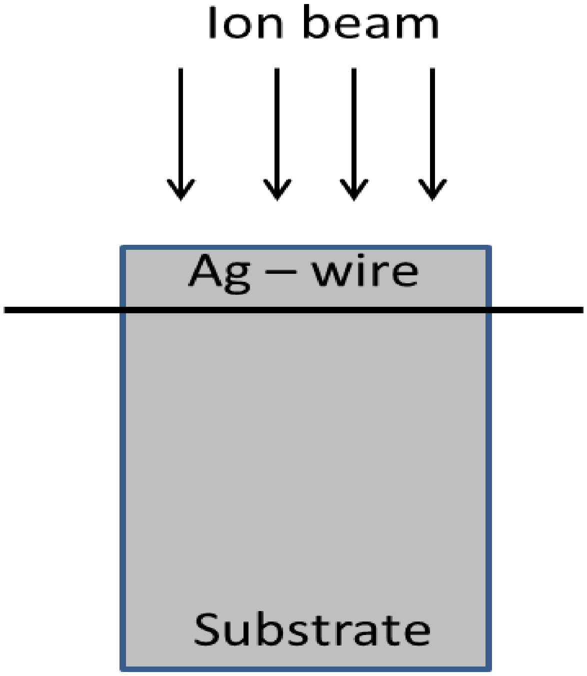

Figure 1: Schematic of placing Ag wire on the Ge substrate during the Si ion bombardment. The arrow indicates the ion-beam direction.

The present investigation employed single-crystal (100) Ge substrates with a resistivity exceeding 30 Ω-cm and a thickness of 0.5 mm. They were cut into pieces with a size of 10×10 mm^2. The samples are irradiated at room temperature with mass-analyzed 26 keV Si^{-} ions in a low energy negative ion implanter equipped with a high current, model PS-120 negative sputter ion source (M/S Peabody Scientific, USA) followed by a sector magnet (Danfysik) for mass analysis. Surface implantation is guaranteed to be free of undesired contamination with the use of a mass-analyzed ion beam. The negative ions minimize the possible voltage built-up on non-conducting samples. The second advantage of negative ion source is free of $^{28}N_2$ molecular contamination. The beam current density was 100 $\mu A/cm^2$. The incidence angle was varied from normal to 60° with respect to the surface normal. To introduce Ag atoms during Si ion implantation a 99.9% pure ~ 0.5 mm diameter Ag wire were attached on the top of sample surface using a special arrangement shown in the schematic figure 1. Ion beams bombarded on the substrates erodes the Ag wire and Ag ad-atoms are re-deposited on the Ge substrate. The ion fluence of all the samples was $1 \times 10^{18}\ ions/cm^2$. After irradiation, the surface morphology of the irradiated samples was examined by scanning electron microscope (SEM) as well as by atomic force microscope (AFM).

III. RESULTS AND DISCUSSION

The AFM images of pristine Ge before any surface treatment and after ion bombardment at different angles and with distinct ion species are depicted in Fig. 1. Fig. 1(a) shows a pristine Ge with no structure. Fig. 1(b) illustrates the formation of pits on the Ge substrate following a 26 keV Si^{-} ion irradiation at a 15° incidence angle with respect to the surface normal. These crater formations persist until incidence angle of 25° is reached. Initially, the aspect ratio of the pit depth and width increases with the increase of incidence angles. However, after 20°, the aspect ratio swiftly decreases, and no pit formation occurs (Figure not shown). As the incidence angle is further increased, a distinct ripple surface is observed at a 60° incidence angle, as illustrated in Fig. 1(c). Although the height modulation of the pit surface is sub-micron, the surface amplitude of the ripple-patterned surface is less than 10 nm. The dot structure on the Ge substrate is illustrated in Fig. 1(d) following bombardment by a 26 $eV\ Au^{-}$ ion. These dot structures persist until an incidence angle of 20°. When incidence angle is further increased beyond 20°, the dots begin to align with a direction that is perpendicular to the projected ion beam direction. The ripple nanostructures formed by a 26 keV Au^{-} ion at an incidence angle of 45° are illustrated in Fig. 1(e). The average wavelength at 45° incidence angle is 209 nm. The dots are ordered perpendicular to the ion beam direction, so the wavy surface has wave vector parallel to the projected ion beam direction. As the wave vector is parallel to the ion beam direction it is called the parallel mode ripple. Figure 1(f) illustrates the perpendicular mode fluctuation of a 26 keV Au^{-} ion at a 60° incidence angle. In all figures from (b) to (f), the ion fluence is 1×10^{18} $ions/cm^{2}$. The average ripple wavelength is 325 nm for Au bombardment at 60° incidence angle.

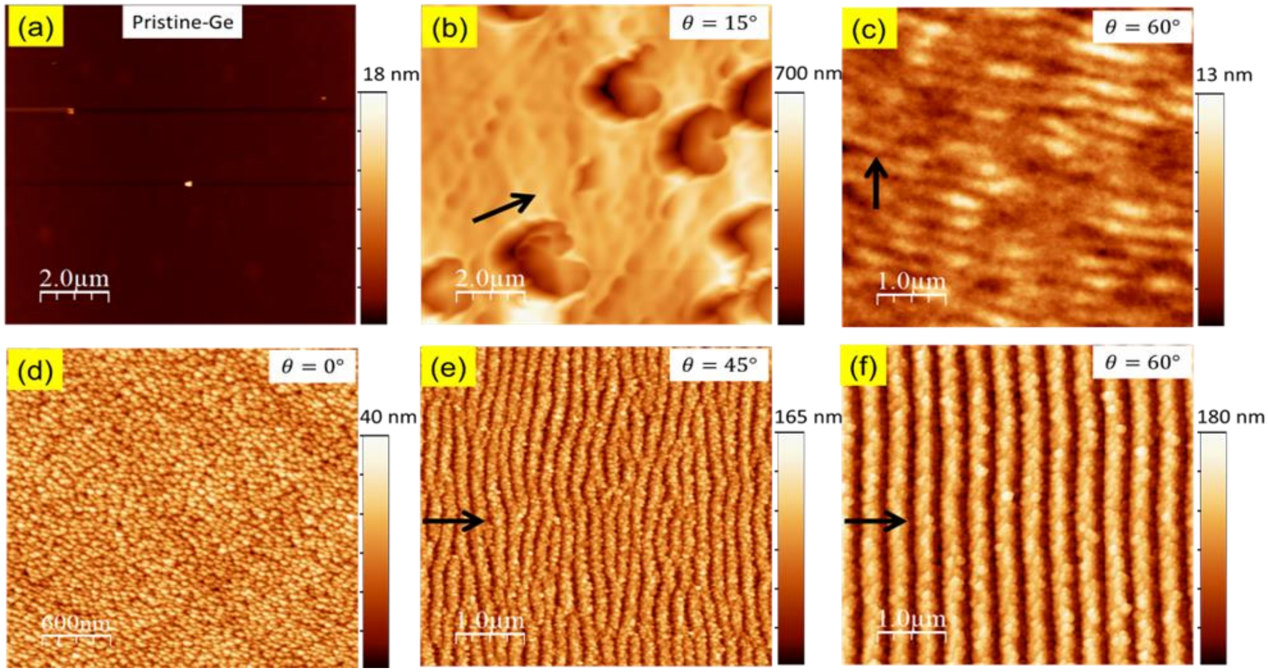

Figure 2: AFM images of Ge substrates. (a) Pristine-Ge before any surface treatment, (b) - (c) Ge substrate after 26 keV Si ion bombardment, (d) -(f) Ge substrate after 26 keV Au ion bombardment, insets in the figure shows incidence angle during ion bombardment

In essence, the ion-induced surface morphology is the outcome of a competition between the roughening and smoothening processes in presence of different type of diffusions that occur during the ion implantation process [9]. During the sputtering process at room temperature, an amorphous layer is formed, and some dispersed atoms redeposit and diffuse, resulting in defects such as interstitials and vacancies [18]. The formation of pits on the Ge substrate during the Si^{-} ion implantation is significantly influenced by these vacancies and interstitials. The Si atoms that have been implanted may establish a more robust Si-Ge bond in comparison to the Ge-Ge bond that has replaced a portion of the Ge-atoms [19]. The stress generated by these Si impurities in the near surface amorphous layer has the potential to generate fractures during high fluence ion implantation [20]. The size of the pits increases as the ion fluence increases. The formation of the pit structure may be contingent upon the presence of an incident ion beam flux that is suitably high. With the increase of incidence angle sputtering increases resulting low implantation of Si atoms inside the Ge top amorphous layer. In contrary to the case of Si ion bombardment Au ion beam produces dot structures at near normal incidences and highly ordered structures at near maximum sputtering angle. Mollick et al. attributed the Au atoms' increased penetration depth into the Ge substrate to a local melting effect that occurred during energetic Au^{-} ion bombardment [4]. Despite the fact that Au does not readily combine with Ge atoms, the presence of a eutectic phase between Au and Ge results in a local melting and spatter cooling process that causes recrystallization at the topmost ion implanted layer [21]. The melting temperature of the Au-Ge mixture decreases to 361 °C during the eutectic phase. These gold atoms, which penetrate beyond the projected range, serve as precursors for the formation of multicrystalline structures in the ion-irradiated layer during ion implantation. The gold seed present at the modified layer generates a modified stoichiometry at the near surface area. The high morphologically ordered nanostructured surface is formed by the coupling of surface height with modified stoichiometry. As the Si does not form any eutectic phase with Ge atoms Si as impurities inside the Ge matrix does not affect any ordering of morphological structures.

Introduction of Ag atoms at the upstream of the ion beam during Si ion implantation on Ge substrate amplitude of surface morphology increases. Ag-Ge atoms possess a eutectic phase. Ag and Ge have melting temperatures of 960 and 949 °C, respectively. The eutectic temperature of a Ge-Ag mixture is 650 °C.

Because of large feature size in Ag-assisted Si ion bombarded Ge substrate AFM image was not captured. The SEM images of the Ag-introduced Si ion implanted Ge substrate at a 60° incidence angle are depicted in Fig 3. The SEM images were acquired from a region approximately 2 mm distant from the Ag wire's location. The silver wire was sputtered and re-deposited on the substrate, contaminating the Ge substrate with Ag atoms, when the ion beam is irradiated with the silver wire at the upstream. A cone-like structure that is elongated along the ion-beam direction is depicted in Figure 3(a). The nanostructured surface is depicted in close-up detail in Figure 3(b). There are cone-like structures with needle-shaped finer structures, as well as perpendicular mode ripple structures that surround the cone structure. The opposite side of incoming ion beam is largely featureless due to shadowing effect. The structures are only a few micrometres in size. An energy dispersive x-ray (EDX) spectrum of the Si ion implanted Ge substrate is depicted in Figure 3(d). The EDX spectrum does not contain any Ag atoms. When bombarded by Si ions in the absence of any additional impurities, the Ge substrate maintained a planar or very low amplitude ripple structure.

SEM images were taken from a region of ~ 2 mm away from the location of Ag wire. When ion beam are irradiated placing the silver wire at the upstream, silver wire were sputtered and re-deposited on the substrate contaminating the Ge substrate by Ag atoms. Figure 3(a) shows a cone-like structures elongated along the ion-beam direction. Figure 3(b) shows a close-up view of the nanostructured surface. There are cone like structure with needle shaped finer structure as well as perpendicular mode ripple structure surrounding the cone structure. The dimensions of the structures are few micrometres in sizes. Figure 3(d) shows an energy dispersive x-ray (EDX) spectrum of the Si ion implanted Ge substrate. No Ag atoms are observed in the EDX spectrum. Ge substrate remained flat or very low amplitude ripple structure when bombarded by Si ion without any additional impurities. When Ag wire is affixed to the surface of the Ge substrate during Si ion bombardment, sub-micron-sized nanostructures with high amplitude and

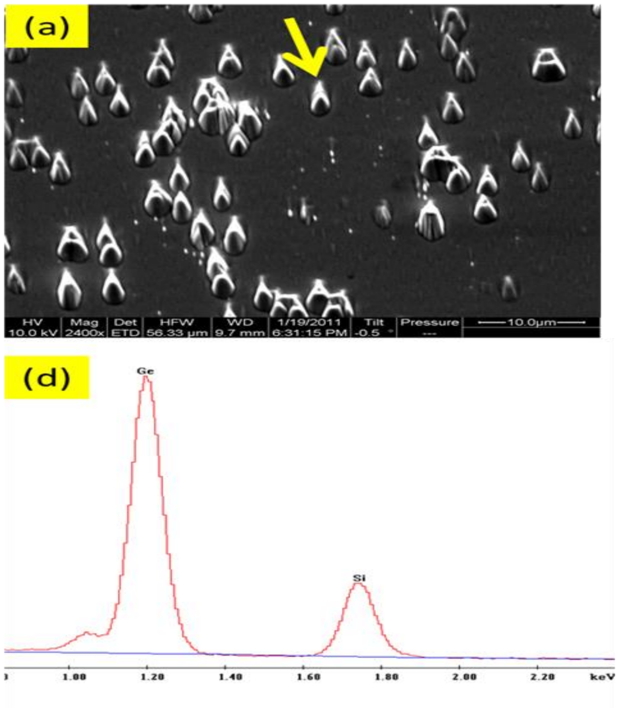

Figure 3: SEM of Ag-assisted nanostructure by 26 keV Si ion at 60 incidence angle. (a) shows a surface that is roughly at a distance of 2 mm from the line where Ag wire were fixed, large number of cone structures are visible, (b) shows a close up view of the cone structures, (c) a further zoomed image shows parallel mode ripples surrounding the cone structures, (d) EDX spectrum of nanostructured Ge substrate

large dimensions are generated. The Ag atoms that are sputtered and re-deposited during Si ion bombardment may serve as precursor atoms for the evolution of morphological structures. The structures are forming with the introduction of Ag atom during the Si ion implantation process; however, the ordering and periodicity of the structures are deficient. However, when Ge substrates are bombarded by Au atoms, highly ordered structures are readily formed. The Ag ad-atoms may serve as seeding atoms to initiate the topographical structures; however, the stoichiometry may not be optimized for a eutectic Ge-Ag mixture to generate a highly ordered periodic structure.

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IV. CONCLUSION

In conclusion, I have observed that pit structures at near-normal incidence angles transition to a flat smooth surface or a ripple surface with a very low amplitude at higher incidence angles. The eutectic phase of the Au-Ge mixture enables the Au-implanted Ge substrate to generate a ripple surface with a high amplitude. These structures are highly ordered and exhibit a high degree of periodicity. Ordered structures cannot be generated by Si ion bombardment alone on the Ge surface. The eutectic phase with modified stoichiometry is essential for the ordered structures, despite the fact that Si impurities may nucleate low amplitude ripple structures. The nanostructure formation on the Ge substrate is once again influenced by the presence of Ag atoms during Si^- ion bombardment. Ag-assisted nanostructure formation is the term that can be used to describe these structures. In order to gain a more comprehensive understanding of the controlling mechanism of Ag-assisted nanostructuring on Ge substrate by Si ion bombardment, additional detailed studies are necessary to adjust various experimental parameters.

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