

Molten target sputtering: Non-conventional method for high mobility Si_{0.15}Ge_{0.85} growth at 500°C

Hyun Jung Kim

National Institute of Aerospace (NIA), 100 Exploration Way, Hampton, VA 23662

ABSTRACT

Since electrons travel over 100 times faster in Silicon-Germanium (SiGe) than in pure Si due to the low effective masses associated with Ge and SiGe-based devices continue to replace Si-based solid-state electronic devices. SiGe thin film on sapphire was successfully grown at 890°C, using a magnetron sputtering system within heteroepitaxial framework. However, SiGe growth at 890°C is a costly and difficult process to produce as a uniform wafer for semiconductor device manufacturing due to thermal soak times, and geometric thermal shadowing from the wafer holder. To leverage the semiconducting capabilities of SiGe, novel processing techniques for SiGe film growth with decreased thermal loading are required.

This paper introduces the Molten Target Sputtering (MTS) method that produces high mobility SiGe on sapphire below 500°C. This non-conventional method has the advantage of high kinetic energy, high-energy latency, and high flux density of sputtered atoms by combining benefits of both magnetron sputtering and thermal evaporation. For the MTS method, a 1~2 mm (depth and width) ring-shaped groove was cut between the center magnet and surrounded by electromagnets creating a circular cavity between the copper plate and source target materials that melt the target material. The SiGe grown from the MTS shows continuous morphology and 99.7% single crystal Si_{0.15}Ge_{0.85} films. The Hall electron mobilities of the Si_{0.15}Ge_{0.85} are 456 cm²V⁻¹s⁻¹ and 123.9 cm²V⁻¹s⁻¹ at 5.59 x 10¹⁸ cm³ and 3.5 x 10²⁰ cm³ carrier concentration at 22.38°C, respectively. This is approximately 5.5 times higher than that of Si and similar to the Ge value at equivalent carrier concentrations and temperatures.

Keywords: Molten Target Sputtering, non-conventional method, high mobility SiGe, below 500°C substrate temperature

The demand for high-tech devices such as smart phones, tablet PCs, security systems, and other advanced electronic hardware relies on high-speed processors for computing. The performance of traditional silicon chips scales by fitting more and more transistors into a constant area or volume of silicon. However, there is a limit to the amount of usable structure that can be incorporated into a silicon wafer. Therefore, a new paradigm is needed to continue to improve the performance of solid-state electronic devices. One promising concept is to use silicon-germanium ($\text{Si}_{1-x}\text{Ge}_x$) alloys to make the next generation CPUs. High Ge composition ratio single crystal $\text{Si}_{1-x}\text{Ge}_x$ on a dielectric substrate is a promising material for high-speed electronic devices including heterostructure bipolar transistors (HBT) for high-speed computing and high electron mobility transistors (HEMT) [1-3]. Although SiGe can theoretically provide semiconductor devices with better performance than Si-based devices, fabricating high quality SiGe is technically challenging. For example, the low Ge-content $\text{Si}_{1-x}\text{Ge}_x$ layers, islands, or twin crystal structures reduce electron mobility beyond that of single crystal Si. This is due to the voids and grain boundaries from lattice mismatching between the substrate and the host materials that slow the charge carrier movement below that of quality Si single crystal films [4,5]. Recently, researchers have demonstrated 99.9% single crystal [111] $\text{Si}_{0.15}\text{Ge}_{0.85}$ films on trigonal *c*-plane sapphire substrate in continuous and smooth morphology [6]. The growth process is described in detail in the Appendix. However, the film growth requires high operational temperature to energize the cubic SiGe structure enough to be rotated and deformed into strained cubic anchored on a trigonal substrate of sapphire. A new method to grow such a super heteroepitaxy at a lower substrate temperature has been implemented by energizing the atoms in flux allowing for reduction of the substrate temperature to a moderate level, below 500°C. The sufficiently energized atoms provide the essential energy needed for the epitaxy process, which deforms the original cubic crystalline structures into a strained structure by physically aligning the crystal structure of both materials at a lower substrate temperature. The newly developed method differs from conventional method.

Molten Target Sputtering for single crystal SiGe on sapphire at 500°C

The requirement of Ge melt over the 890°C substrate temperature hinders the widespread application of SiGe because of issues related to geometric thermal shadowing from the wafer holder and total processing time. In order to continue to improve semiconductor quality, novel processing technique for producing the SiGe film with less thermal loading and shorter times is required. The novel processing technique needs to be a different method of providing sufficient energy to the incoming atoms. Since the energy imparted to atoms determines their kinetic energy and

elevates the energy latency for the degrees of freedom to readily reconfigure when they arrive at a substrate, it is important for these atoms within a diffusion plasma to be preloaded with sufficient energy.

This paper describes the Molten Target Sputtering (MTS), a new method to realize the high deposition rate of continuous high Ge-content $\text{Si}_{1-x}\text{Ge}_x$ films on sapphire substrates with 500°C substrate temperature, from the Ge being in the melt-state, while Si is not. The fundamental concept of MTS is described as follows. During conventional magnetron sputtering, evaporation can be created using a thermal-isolated target from cooling elements of the sputtering gun assembly. When the thermal energy that is released in the surface layers under the plasma is kept in the target and the energy is enough to melt the target, an intense evaporation is occurred. The evaporation-involved sputtering from the molten target enables enhancement of diffusion mobility of atoms, which results in an improvement of surface morphology from the high power density of molecules ($\leq 55\text{W}/\text{cm}^2$ (cold target), $55\sim 75\text{W}/\text{cm}^2$ (hot target), and $\geq 75\text{W}/\text{cm}^2$ (molten target)) compared to the conventional sputtering with solid target [7-9]. The MTS provides a high deposition rate of the coating, through the high flux density of Ge molecule during evaporation are evolved from the target more effectively than by sputtering, because the MTS is uses ionized molten target to get benefit from both sputtering and evaporation [Supporting Information 1].

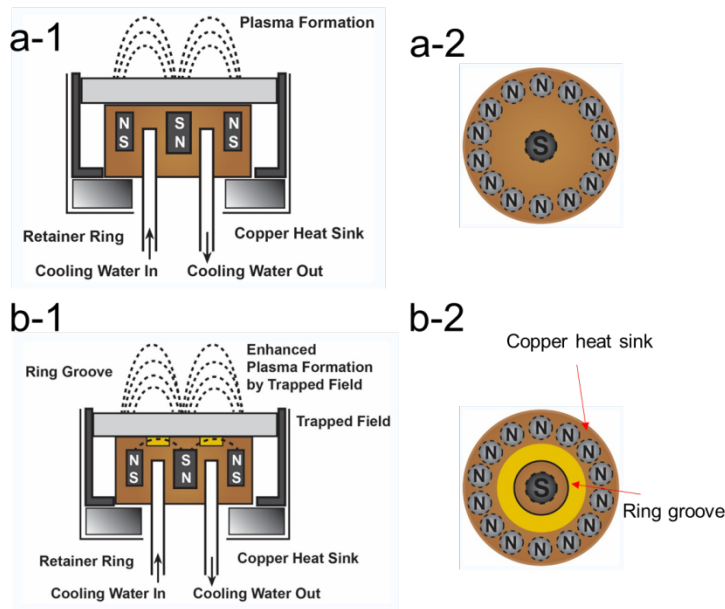


Figure 1. Side and top view schematics of conventional magnetron sputtering and modified magnetron Molten Target Sputtering (MTS) gun. (a) conventional magnetron sputtering: side view (a-1) and top-view (a-2)

of conventional magnetron-sputtering gun. (b) molten target sputtering: side view (b-1) and top-view (b-2) of the MTS gun. The top-view of MTS gun shows a ring groove for the partial heating of the target material.

Figure 1 depicts the side and top views of conventional magnetron sputtering (a-1, a-2) and the modified magnetron sputtering gun used to melt the Ge source target (b-1, b-2). The physical difference between the two guns is the ring groove on the copper heat sink plate. This modification on the gun from the thermal-isolation allows the solid target material to melt, so the new system is named Molten Target Sputtering (MTS). For the MTS method, the ring-shaped groove (marked by yellow) with the dimension of 1~2 mm both in depth and width was cut between the magnets in order to keep a gap between the copper plate and the sputtering source target as shown in (b-1) and (b-2). The heat increases on the target material surface from this gap because of the conduction passage of the thermal energy to a water-cooled copper sink removed by the void (yellow) below the target. Accordingly, the target surface is additionally heated and melts. The magnetic arrangement, where one pole is positioned at the central axis of the target and the opposite pole is circumferentially placed around the outer edge of the target, confines the electrons along the magnetic flux lines near the target (figure 1 (a-2) and (b-2)). The $\text{Si}_{1-x}\text{Ge}_x$ composition ratio depends on the DC power applied to each sputtering gun, and the ratio of constituent fluxes remains stable and consistent during the deposition indicated by thickness monitoring. The reduced thermal mass of the target material also works to keep the target surface in a molten state. Through numerous tests, it was found that the target with less than 3~5mm thickness works better to melt the surface.

The ring groove in the new gun design improves not only (1) the flux density but also (2) the kinetic energy of molecules at the target. By raising the temperature of the target materials, (1) the number of detached atoms and molecules from the target is increased, and (2) the detached atoms gain more energy from the molten target materials than was achieved with the conventional sputtering process. The ring-shaped groove between magnets traps a portion of the magnetic field, providing additive force to eject the ionized particles within the plasma, resulting in an increase in kinetic energy versus the conventional sputtering process.

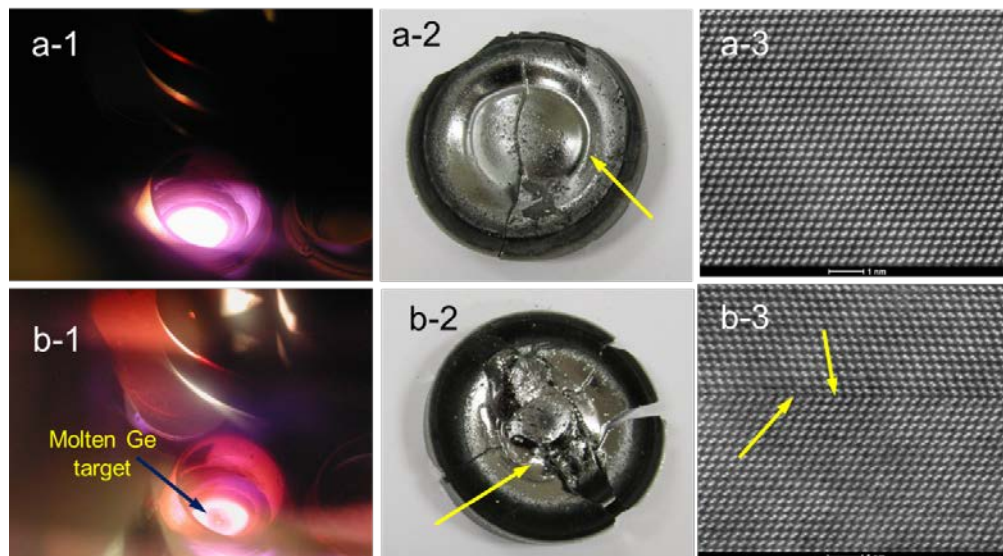


Figure 2. Target material differences between the conventional magnetron sputtering and the molten target sputtering. Photo of plasma from general sputtering on solid target inside the sputtering chamber (a-1). Photo of the sputtered solid target with a trace (indicated by arrow) after the conventional magnetron deposition (a-2). HRTEM image of the sputtering target after the conventional sputtering process (a-3). Photo of plasma from the molten target inside the sputtering chamber (b-1). Photo of the molten and solidified target with plasma trace and irregular shape (indicated by arrow) after the molten target sputtering process (b-2). HRTEM image with the twin crystal structures (indicated by arrow) from the molten target sputtering process (b-3).

Figure 2 shows target material differences between the conventional magnetron sputtering and the molten target sputtering. The plasma ring around the magnet equator from the molten sputtering target (b-1) looks heterogeneous versus the conventional process (a-1) and the wavy zone of target is indirect evidence of the liquid state of the target, and the high flux density of molecules. The deposition rate from the molten target sputtering was approximately 10 times higher than the conventional sputtering from the solid target, and was monitored by a thickness monitor during the deposition. This was the direct evidence that the liquid state of the target had higher flux density of molecules than the solid target [Supporting Information 2]. The sputtered target in (a-2) shows a trace of solid target after the conventional magnetron deposition. The glow discharge plasma stabilized with the assist of the circumferential magnetic field from the imbedded magnets inside the copper heat-sink. The target from the molten sputtering in (b-2)

shows a mixture of the plasma trace and irregular shape as indicated by the yellow-arrow. The plasma trace on the molten target comes from the recycled solid target after the conventional sputtering process before the molten process.

The deposition rate of the SiGe film increases by increasing target power density, which is connected to the heating of the sputtered target. The cold target with 1/8" thickness of the Ge target material is gradually converted to a hot target, and to a molten target as target power density increases: $\leq 55\text{W/cm}^2$ (cold target), $55\sim 75\text{W/cm}^2$ (hot target), and $\geq 75\text{W/cm}^2$ (molten target) [8-10]. The high-resolution transmission electron microscopy (HRTEM) image of the Ge target from the molten target sputtering process shows twin crystal structures as indicated by yellow-arrows (b-3) which is not shown in the target from the conventional sputtering process (a-3) [Supporting Information 2 and 3]. As shown in these photos, the molten target material releases more high latency atoms that carry sufficient energy towards the substrate for facilitating the formation of a modified crystal structure, from a cubic to a strained structure until fully relaxed.

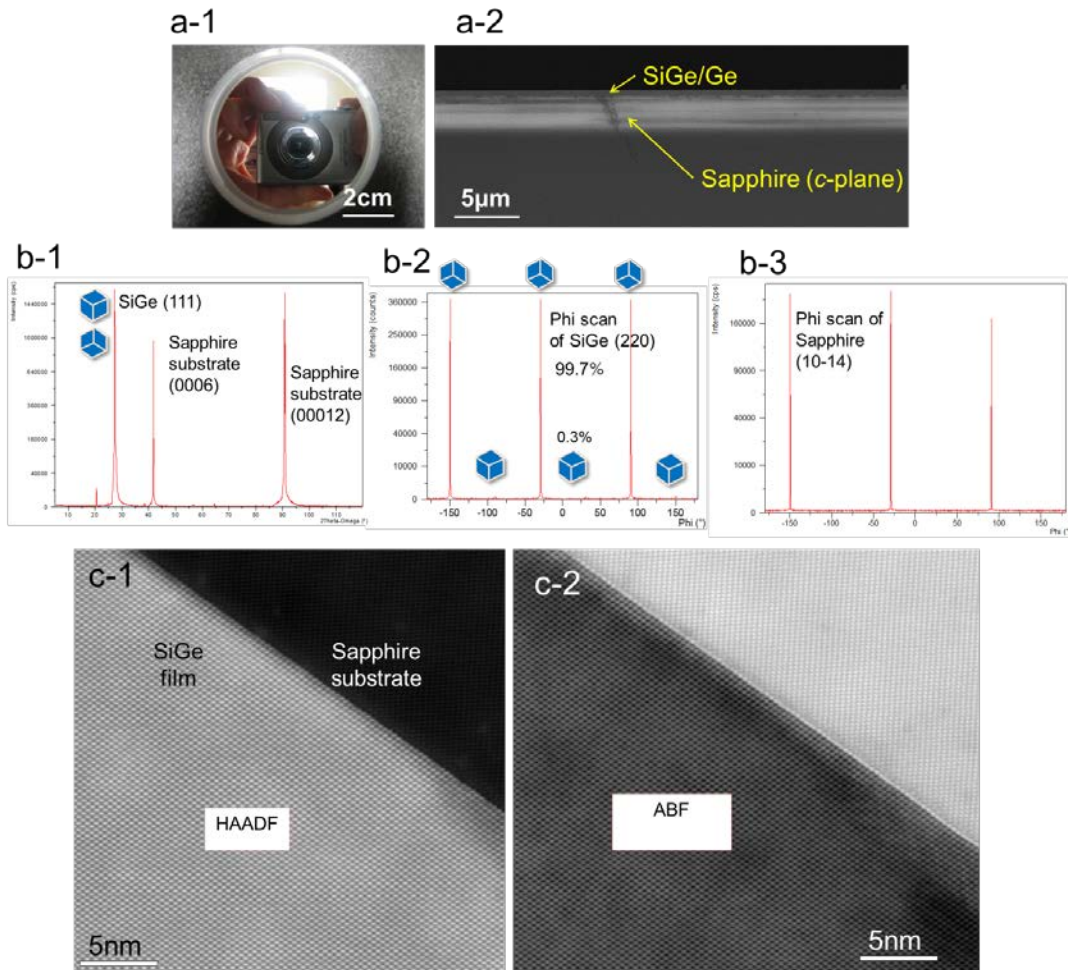


Figure 3. Crystallinity of SiGe on sapphire (Al_2O_3) film grown by molten target sputtering. Photo of SiGe with mirror-like surface (a-1) and cross-section of SEM image of the same sample (a-2). Symmetric θ - 2θ XRD scan shows only the SiGe (111) reflection at $2\theta \sim 27.6$ degrees along with the Al_2O_3 (003), (006), (009), and (0012) reflections (b-1). SiGe (220) scan shows three strong reflections (offset by 120 degrees) with three small reflections rotated 60 degrees from them indicating greater than 99.7% in-plane orientation of the SiGe (b-2), and sapphire ($10\bar{1}4$) scan show three strong reflections (a-3). HAADF (High-Angle Annular Dark-Field) image of the SiGe and sapphire interface (c-1). ABF (Annular Bright Field) image of the SiGe and sapphire interface (c-2).

Figure 3 (a-1) shows the photo of wafer with a mirror-like surface. The SiGe on Al_2O_3 was a continuous smooth film as shown in Figure 3 (a-2). X-Ray diffraction (XRD) data of these highly single crystalline (>99.7%) SiGe layers on *c*-plane sapphire wafers are shown in figure 3 (b). A symmetric θ - 2θ scan, which probed the surface normal direction of the sample, showed only the SiGe (111) reflection at $2\theta \sim 27.5$ degrees along with the Al_2O_3 (003), (006), (009), and (0012) reflections [**Supporting Information 4**]. No other SiGe reflections, such as the (220), (311), or (400), appeared in the symmetric scan, verifying that all of the crystallites were oriented in the [111] direction. The in-plane orientation of the crystallites was measured with a scan of the SiGe (220) reflections. Three strong reflections, offset by 120 degrees in the scan, indicated the majority in-plane orientation of the SiGe with three small peaks indicating the 60 degrees rotated (twinned) minority in-plane orientation. The majority percentage of the SiGe crystallites was determined by comparing the integrated areas under each peak. Single crystalline SiGe layers greater than 99.7 percent were fabricated in these growth runs according to these XRD measurements shown in Figure 3. 4k x 4k STEM images (figure 3 (c)) provide a field of view with high resolution detail of no twin and highly crystalline SiGe film grown on *c*-plane sapphire. The epitaxial relationship between the SiGe film and the sapphire structure is (111) SiGe // (0001) Al_2O_3 and [011] SiGe // [01 $\bar{1}$ 0] Al_2O_3 .

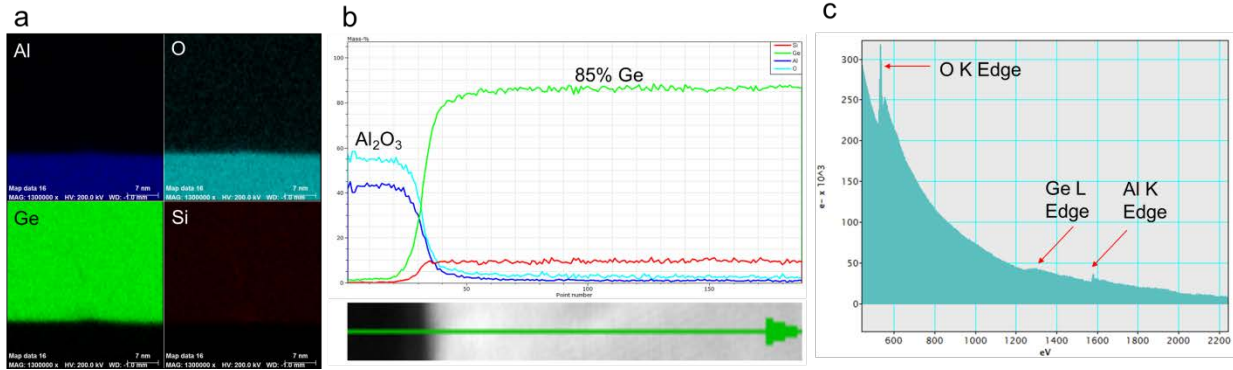


Figure 4. Composition ratio of SiGe on sapphire (Al₂O₃) film grown by molten target sputtering.

Quantitative STEM-EDX mapping (a) and line scan of EDX mapping of SiGe film (b). Si and Ge uniformly distributed in the film and 85% of Ge concentration confirmed by EDX line profile of the film. Total EELS signal of SiGe film (c) o Si K edge is visible from the total EELS signal due to fast acquisition and relatively lower concentration of Si.

Figure 4 (a) and (b) show the TEM mapping and quantitative line scan of STEM- Energy Dispersive X-ray (EDX) mapping. The mapping shows the Si, Ge, Al, and O elements and homogenous SiGe with 85% of Ge concentration [Supporting Information 4]. The total EELS signal of the SiGe film shows no Si K edge due to fast acquisition and relatively lower concentration of Si (c).

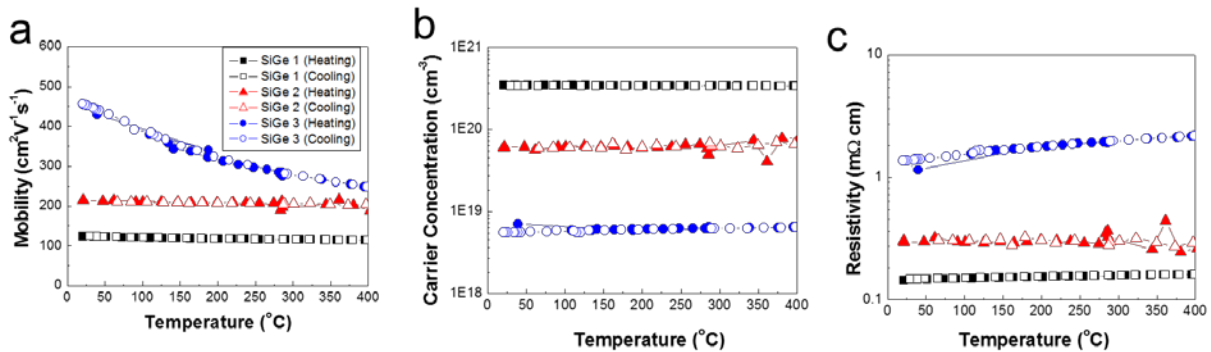


Figure 5. Mobility, carrier concentration, and resistivity of SiGe film. (a) Hall electron mobility (μ) as a function of temperature (both heating and cooling) for three samples with different amount of boron (B) doping

(denoted SiGe 1, SiGe 2, and SiGe 3). (b) Carrier concentration (n) as a function of temperature for the same three samples. (c) Resistivity of the same three samples as a function of temperature.

Figure 5 shows the Hall mobilities, carrier concentrations, and resistivities as a function of temperature, both heating and cooling, and boron doping concentrations. The highest mobility, $456 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 22.38°C occurs for a carrier concentration of $5.59 \times 10^{18} \text{ cm}^{-3}$. This mobility is about 5.5 times higher than that of the Si given by Masetti *et al* and similar to the Ge value at equivalent carrier concentrations in Figure 5 (a) [11-13]. Both hole mobility and resistivity of (1) $3.5 \times 10^{20} \text{ cm}^{-3}$ carrier concentrations are $123.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $0.146 \text{ m}\Omega\text{cm}$, (2) $6.11 \times 10^{19} \text{ cm}^{-3}$ carrier concentrations are $214.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $0.296 \text{ m}\Omega\text{cm}$, (3) $5.59 \times 10^{18} \text{ cm}^{-3}$ carrier concentrations are $456 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $1.36 \text{ m}\Omega\text{cm}$ at 20°C , respectively as summarized in Table 1. $5.59 \times 10^{18} \text{ cm}^{-3}$ carrier concentration SiGe film exhibits a gradual decrease with increasing temperature but not the two other samples with higher carrier concentration. This may imply that carrier mobility is independent of temperature in the heavily impurity-doped SiGe with such relatively high Ge contents. There was no success in measuring the Hall mobility of SiGe films grown by the conventional sputtering at 500°C , due to discontinues film morphology.

Table 1| Hole mobility and resistivity based on the carrier concentration

Si / Ge ratio of $\text{Si}_x\text{Ge}_{1-x}$	Substrate temperature ($^\circ\text{C}$)	Carrier concentration (cm^{-3})	Hole mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Resistivity ($\text{m}\Omega\text{cm}$)	Measure temperature ($^\circ\text{C}$)
$\text{Si}_{0.15}\text{Ge}_{0.85}$	500	3.5×10^{20}	123.9	0.146	20
$\text{Si}_{0.15}\text{Ge}_{0.85}$	500	6.11×10^{19}	214.4	0.296	20
$\text{Si}_{0.15}\text{Ge}_{0.85}$	500	5.59×10^{18}	456	1.36	20

It is not possible to compare the hall mobility with films grown by a conventional sputtering system at an identical substrate temperature, 500°C , because of the difficulty in measuring this value due to discontinuities in film morphology. The high Hall mobility of SiGe grown by MTS is further evidence for low defect densities and smooth film surface. Figure 5 (b) shows the carrier concentrations as a function of temperature for the SiGe films. The slight increase in carrier concentration up to 400°C has been observed for $6.11 \times 10^{19} \text{ cm}^{-3}$ boron-doped SiGe samples only. The concentrations of the low and high impurity-doped crystals are almost independent of temperature up to 400°C .

CONCLUSIONS

Single crystal SiGe on sapphire was grown at high substrate temperatures, 890°C, to get the structure deformation energy of SiGe to align on the sapphire substrate. This process requires long thermal loads and long soak times of the substrate at high temperature, making this impractical for commercial mass production. In order to continue to improve semiconductor performance and efficiency from the advantage of high mobility of SiGe films, novel processing techniques for producing the SiGe film with less thermal loading effort are required.

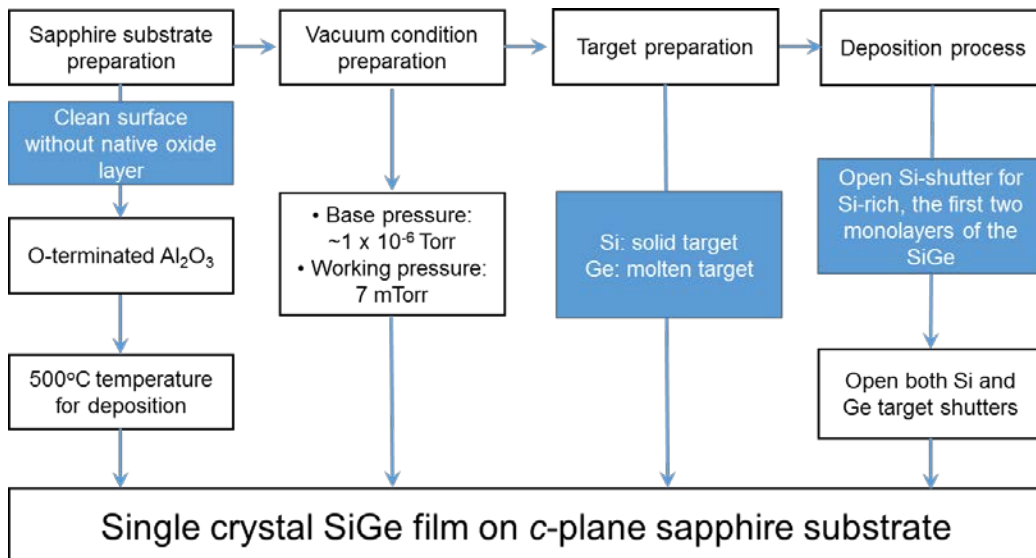
From the previous research, both substrate temperature and power for the magnetron gun are the important variables for single crystal SiGe on sapphire substrates for straining the cubic structure to match to the sapphire substrate and high deposition rate of molecules under heteroepitaxy growth. A new film deposition method, Molten Target Sputtering (MTS), provides high deposition rates of the coating from a high flux density of Ge molecule, during evaporation are evolved from the target more effectively than by sputtering because the MTS is not evaporation but also ionized evaporation.

The SiGe grown from the MTS shows continuous morphology and 99.7% single crystal $\text{Si}_{0.15}\text{Ge}_{0.85}$ films. The Hall mobilities of the $\text{Si}_{0.15}\text{Ge}_{0.85}$ are $456 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $123.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at $5.59 \times 10^{18} \text{ cm}^{-3}$ and $3.5 \times 10^{20} \text{ cm}^{-3}$ carrier concentration at 22.38°C, respectively that is higher than that of the Si and similar to the Ge value at equivalent carrier concentration and temperature.

The MTS can be applied for heteroepitaxy framework film growth that requires a high substrate temperature for structure deformation to match to the substrate lattice parameter.

METHODS

Sample preparation and film deposition: A 2-inch *c*-plane sapphire substrate (1-side polished, MTI Corporation) was cleaned to obtain a surface without native oxide layer or organic and inorganic contaminants, such as the chemical mechanical polishing (CMP) slurry by using acetone (ACS grade), iso-propanol (ACS grade), and deionized water sequentially before deposition. The cleaned sapphire wafer was loaded on a molybdenum wafer holder with the epi-ready side facing downward in the bottom-target design sputtering chamber. The wafer was preheated by using a PBN / PG (Pyrolytic Graphite) ceramic heater (Momentive Inc.) through two-steps (200°C and 1000°C) at the base pressure of the sputtering chamber, 1×10^{-6} Torr. The sapphire wafer was baked at 200°C for 20 minutes to remove water vapor, any volatile contaminants, and native oxide layer. After this, the wafer was heated to 1000°C for another 60 minutes to desorb any oxygen atoms [14,15]. To prevent thermal shock and wafer cracking, the substrate ramped to 1000°C with the increment of 5°C/minute. The pressure for the SiGe film deposition was 7mTorr with a 5 sccm of high-purity, research grade Ar (99.9999%) flow. The Si (undoped, 99.999%, Kurt J. Lesker) target-loaded magnetron gun ran at 200W and Ge (n-type, 5-40 $\Omega \cdot \text{cm}$, 99.9999%, Kurt J. Lesker) target with 3~5 mm thickness was melted by the MTS process. The Si target shutter opened for 5 minutes for the pre-sputtering of the initial Si-rich monolayers of SiGe, and was followed by the opening of the Ge shutter. For the mobility test, the boron target with 1~3W RF power was co-sputtered during the SiGe film deposition process, which resulted in heavy doping above $10^{19}/\text{cm}^3$. During the 30 minutes deposition, the growth rates of both Si and Ge were monitored from the quartz thickness monitor (Maxtek, Inc.) as 0.7 Å/minutes and 10 Å/minute, respectively.



Photography and SEM: The photography images were taken by using a Canon Powershot SD400 5MP Digital Elph Camera. The SEM cross-section of SiGe on sapphire was taken from the SEM (JSM-5800).

XRD characterization: The SiGe film was scanned with a Panalytical X'Pert Pro XRD system along the 2θ - ω and phi (Φ) scan. The vertical atomic alignment was measured with a symmetric 2θ - ω scan, which probes the surface normal direction from 5 to 120° to establish overall film quality. The majority percentage of the SiGe crystallites was determined by comparing the integrated areas under each peak. The Φ scan is parallel with the (111) SiGe surface normal, and each scan completed one whole revolution of the wafer at a constant position designed to find all the {220} reflections. A similar Φ scan is done with the sapphire (0001), parallel with the (111) SiGe surface, to find all the $\{10\bar{1}4\}$ reflections [16-18]. A high quality SiGe film will have three peaks in the SiGe scan, corresponding to the three {220} planes in the film. The presence of six peaks, 60° offset from one another, corresponds to two twins, rotated 60° with respect to one another, each with three {220} reflections. Relative peak heights of these twins are compared to determine how much of each twin exists in the SiGe film.

TEM sampling and TEM characterization: TEM samples were prepared using a FEI Quanta 3D FEG focused ion beam (FIB) [19]. The interface between SiGe and Al₂O₃ was characterized using an FEI Titan 200kV TEM. An aberration-corrected scanning transmission electron microscope (STEM) equipped with a high-angle annular dark field (HAADF) detector and an annular bright field (ABF) detector, and an energy-dispersive X-ray spectroscopy (EDX) were used to analyze the atomic structure of SiGe specimen. All the TEM images and EDX mapping images were collected using a 200kV acceleration voltage. The STEM image was obtained with an 18 mrad convergence angle using 50 μ m C2 aperture. The HAADF STEM image was developed using Fischione HAADF and FEI DF4 detectors. The ABF STEM image was obtained using a combination of FEI DF4 / DF2 detectors after adjusting the suitable camera length. The EDX was used to detect the chemical element distribution of the SiGe / Al₂O₃ interface. In this method, a coherent focused probe scanned across the specimen, and the resultant x-ray emission spectrum was recorded at each probe position. These spectra were then used to construct an elemental line scan. The acquisition time for a $\langle 112 \rangle$ zone-axis of SiGe on sapphire EDX mapping was 11 minutes under a 512 \times 512 pixel image size, 250pA beam current, and spot size of 6. The Electron Energy Loss Spectroscopy (EELS) has been performed over a range of 400 ~ 2300eV.

Hall-effect measurements: The Hall mobility, carrier concentration, and resistivity were measured as a function of temperature from room temperature, 20°C to 400°C using a Physical Property Measurement System (Quantum Design) at the NASA-JPL thermoelectric laboratory [20,21]. A square shaped van der Pauw geometry sample (10mm x 10mm), with ohmic contact (<1mm x 1mm) at the sample corners, was used for the measurement, under a reversible 1 Tesla magnetic field.

APPENDIX

Single crystal SiGe on sapphire at 890°C from magnetron sputtering: NIA / NASA researchers exhibit best practice 99.9% single crystal $\text{Si}_{0.15}\text{Ge}_{0.85}$ films in continuous and smooth morphology [6]. A conventional magnetron sputtering system was used for the $\text{Si}_{0.15}\text{Ge}_{0.85}$ film growth at a 890 °C substrate temperature, with 200W DC (~40W/cm², cold target) power supplied to both solid Si and Ge source target, respectively. At an 890°C temperature under 7mTorr working pressure, the Ge on the substrate was melted and. Based on the data analysis of the previous work, several key factors for high mobility SiGe film growth were found [**Supporting Information 5**]. One of the crucial factors for a successful formation was structure deformation of SiGe from cubic to a strained structure [6,16,22-23]. This strained structure is created from the increase in, lattice spacing distance of SiGe while maintaining the cubic crystal structure after the first Si-rich layer on SiGe film aligns over the O-terminated Al_2O_3 substrate. Recently, the thermal expansion calculations between SiGe and Al_2O_3 substrates show that SiGe can form single crystal films in the 450-550°C temperature range, along with increased DC power up to 600W (~59W/cm², hot target) and the 500°C substrate temperature was chosen as starting substrate temperature for this work [22]. The single crystal structure of SiGe was verified by x-ray diffraction (XRD) but atomic force microscope (AFM) images show the film is inferior to, which is another important factor for device application for high mobilities. From these facts noted from the previous research, (i) molten Ge from the higher than 850°C substrate temperature along with the (ii) high deposition rate (flux density) of Ge source target (higher than 200W, ~40W/cm² power density) are important parameters for uniform / continuous single crystal $\text{Si}_{0.15}\text{Ge}_{0.85}$ film growth. Especially, the previous work describes the thermal dynamic energy required for [111]-axis SiGe structure deformation from diamond cubic to strained cubic structures to align with the [0001]-axis of the trigonal structure sapphire. Without the Si and Ge structure deformation, undesirable twins and dislocations generate from the dissimilar crystal structure and the deformation energy comes from the heated substrate of 890 °C, especially with the high Ge-content [7,24-25].

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Supporting Information

Molten target sputtering: Non-conventional method for high mobility $\text{Si}_{0.15}\text{Ge}_{0.85}$ growth at 500°C

Hyun Jung Kim

National Institute of Aerospace (NIA), 100 Exploration Way, Hampton, VA 23662

Supporting information 1.

Molten Target Sputtering (MTS) deposition has special features such as **enhanced kinetic energy** and **flux of ionized atoms**. The following are comparisons with between magnetron sputtering, MTS, and thermal evaporation, with the advantages of MTS highlighted;

1. **High kinetic energy of molecules**: The electron mobility of molecules from the MTS are higher than the ones from the conventional sputtering (5eV) and similar to the thermal evaporation (50eV) ones. The high molecular mobility from the MTS would improve the deposited film quality [1,2].
2. **High flux density of molecules**: MTS generates high plasma density as more electrons come out from the molten target than the solid target. As a result, the deposition speed would be increased from the MTS compared to the conventional sputtering and similar to the thermal evaporation.

The deposition rate from the cold target is controlled by sputtering from the hot target by the combined action of sputtering and sublimation, and from the molten target mainly by evaporation [3]. This is the reason why the deposition rates of the coating deposited from the hot and molten targets are higher than that of the coating sputtered from the cold target. The highest deposition rate of the coating is achieved in the evaporation from the molten target. The deposition of coating from the molten magnetron sputtering is not limited to evaporation, ionized evaporation also occurs since evaporated atoms pass through a magnetron discharge in order to be effectively ionized [3]. Both hot and molten targets are a subject of intensive development in numerous labs as the new sputtering systems have yet to be mastered [3].

3. **Assist the substrate heating**: The energy of the ejected electrons from the sputtering target follows the gun power on the metal target. For example, when 400V is applied to the Ge target during the deposition, individual electrons from the target also contain 400V and move to the substrate along with the Ge molecules for film deposition. The high voltage electrons from the MTS assists the substrate heating and ultimately improve the film quality.
4. **Ionized atoms**: The molecules from the MTS are ionized atoms from the plasma; this is not the same as thermal evaporation

Supporting information 2.

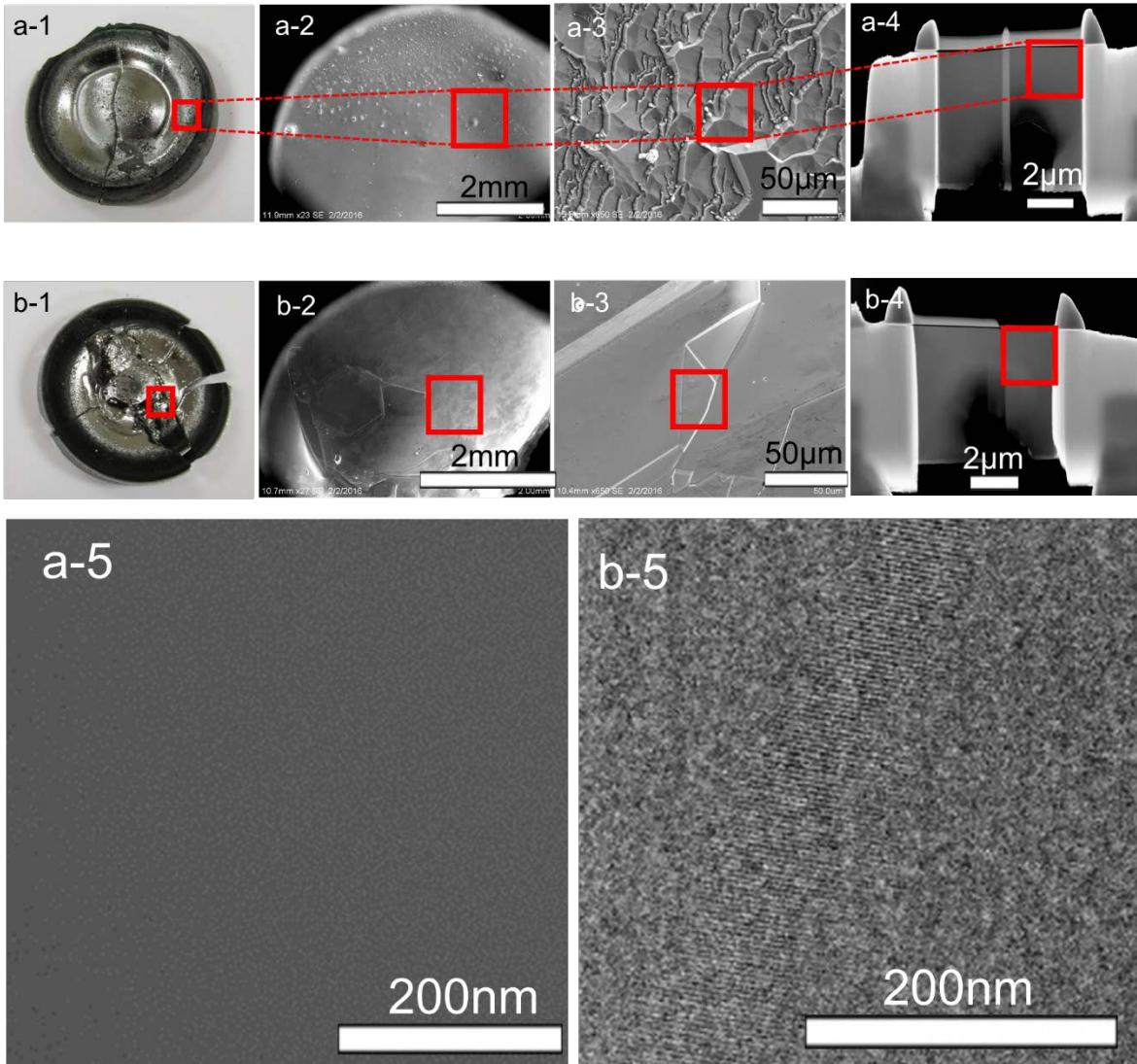
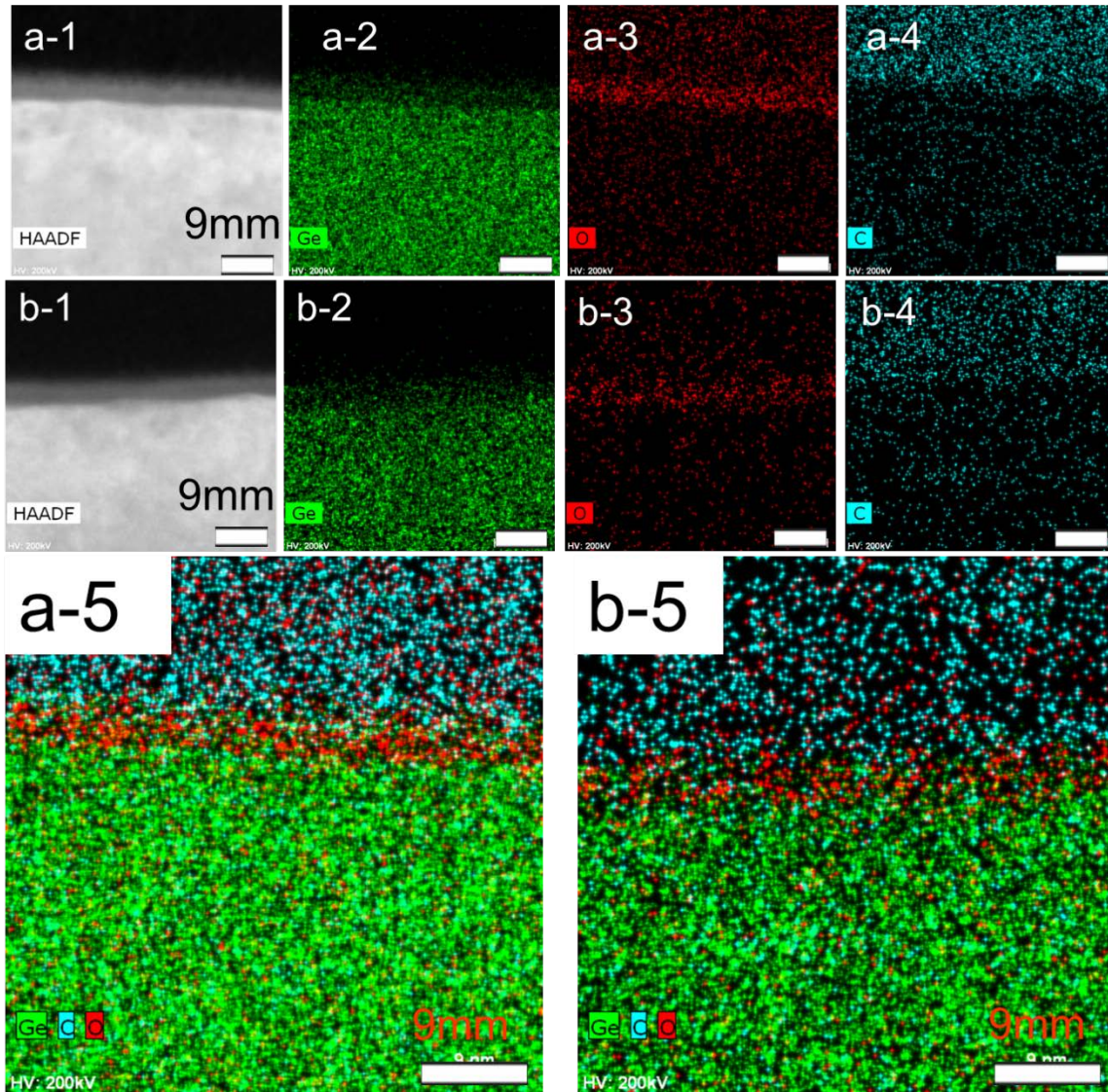


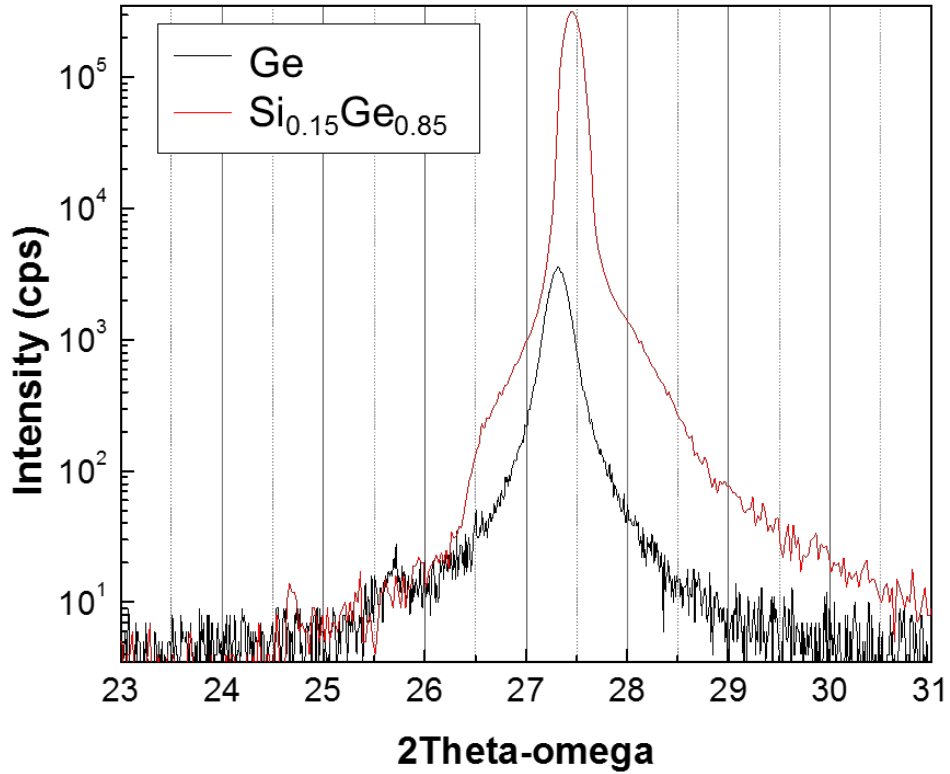
Figure (a-1) and (b-1) are images of the Ge target after sputtering. (a-1) shows the circular groove on the Ge target from the plasma during the conventional sputtering. (b-1) shows uneven shape of Ge target from the MTS. (a-2), (a-3), (a-4) are the SEM and TEM images of the solid Ge target from a conventional sputtering system and (b-1), (b-2), (b-3), and (b-4) are the SEM and TEM images of the Ge target from the MTS. The TEM samples were prepared by focused ion beam (FIB) lithography. The surface of the solid target from the conventional magnetron sputtering is rough and has steps like figure (a-2). On the other hand, figure (b-2) shows the molten target surface is smooth. Figure (a-5) and (b-5) show the HRTEM image of the Ge targets from the conventional sputtering and MTS, respectively. Figure (b-5) shows the twin lattice and stacking faults in the Ge target and supports that the Ge target was melted and then solidified.

Supporting information 3.



EDX mapping of Ge targets after sputtering by using (a) the conventional system and (b) the molten target system (MTS). (a-1) and (b-1) are HRTEM HAADF images of the Ge targets from the conventional and MTS systems, respectively. Element mapping of Ge (a-2 and b-2), O (a-3 and b-3), C (a-4 and b-4) and combined Ge / C / O. The composition ratio is the same between the Ge targets from both conventional sputtering and the molten target sputtering. Both have oxide layers on the Ge target surface.

Supporting information 4.



X-ray diffraction (XRD) 2θ-Ω scan of SiGe (red line) and Ge (black line) grown on the sapphire substrate. By increasing Ge content the (111) diffraction peak in Si_{1-x}Ge_x progressively shifts to lower angles from that of Si in comparison with Ge. The variation in lattice constant follows the general trend of bulk Si_{1-x}Ge_x in Vegard limit [4,5]. These results confirm appropriate alloying of Si and Ge in the SiGe film. The sample has the composition of Si_{0.15}Ge_{0.85}.

Supporting information 5.

The following pertains to the research performed by the author and associates at the NASA Langley Research Center / National Institute of Aerospace which motivated development of the Molten Target Sputtering technique.

(1) *Reference: “Rhombohedral epitaxy of cubic SiGe on trigonal c-plane sapphire”, Y. Park et al, J. Crystal Growth, 310, 2014-2731 (2008)*

Highly [111]-oriented rhombohedral hetero-structure epitaxy of cubic SiGe semiconductor on trigonal c-plane sapphire was characterized by X-Ray Diffraction (XRD).

Temperature [°C]	Power [watt]	SiGe (113) [a.u.]	SiGe (220) peak [Y/N]	FWHM [intensity]	Twin : Single [ratio]	SiGe (111) peak [intensity]
820	150	~20	Yes	0.81	60:40	~10 ⁵
820	200	~50	No	0.17	83:17	~10 ⁵
820	300	~900	No	0.13	92:8	~10 ⁶
>850	200 and 300	~50	No	0.15	0.3:99.7	~10 ⁶

- In order to promote continuous single crystal Si_{0.15}Ge_{0.85} film growth on c-plane sapphire substrate the substrate temperature has to exceed 850 °C substrate temperature, have 200W DC power for both Si and Ge source target, and 7sccm Ar flow with 5mTorr working pressure.

- The orientation relationship between Si_{0.15}Ge_{0.85} and Al₂O₃ is (111)SiGe || (0001)Al₂O₃, [011]SiGe || [01 $\bar{1}$ 0]Al₂O₃

- Both the single and twin SiGe (111) had 60° rotated orientations. The type of twin formed varied between the evaluated 820°C and 890°C fabrication temperatures. The volume percentage of the twins depended on the magnetron sputtering power.

- Increasing the sputtering target power from 150W to 300W with a 820°C substrate temperature, the Full Width Half Maximum (FWHM) intensity was decreased, SiGe (111) peak intensity increased, and twin intensity was increased.

- By increasing the substrate temperature from 820°C to 850°C at 200W DC power, the ratio of single orientation increased, switching the ratio of the majority from twin to single

- Both the substrate temperature and Si and Ge source target power respectively determine the type of the twins and volume percentage of dominant twins.

- In order to fabricate high single dominant with low FWHM, 200-300W DC power and a substrate temperature of >850°C are required, as well as a smooth surface (111) Si_{0.15}Ge_{0.85} film on (0001) Al₂O₃ (c-plane sapphire) substrate

(2) *Reference: “Temperature dependence of crystalline SiGe growth on sapphire (0001) substrates by sputtering”, H.J. Kim et al. J. Crystal Growth, 353, 124-128 (2012)*

The type of twin formed at the two temperatures, 820°C and 890°C varied. The early and final stage morphologies affected by the substrate temperatures from the Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM) characterizations are given below;

Temperature [°C]	Fixed power (watt)	Early stage shape	Early stage size [µm]	Density of particles [relative amount]	Final morphology [description]
820	200	Hemi-spherical caps	~1 (Height) x 1 (Width)	More	Coalescence with many voids
>850 (890)		Mix with (1) pyramidal or triangular shape with smooth surface and (2) hemi-spherical caps	(1) 1~2 (Height) x 10 (Width) and (2) ~1 (Height) x 1 (Width)	Less	Smooth film without voids

- At a substrate temperature of 820°C, (1) early stage of film growth, each island has its own orientation. At the final stage (2) of the film growth, two non-connected islands with 60° twin relationship have formed.
- With the substrate temperature higher than 850°C, (1) early stage of the growth has two islands with 60° twin relationship. At the final stage (2) of the growth, the ratio of the twins was decreased and the surface morphology became smooth without voids or noticeable boundaries
- The volume of twins was suppressed by increasing the growth temperature from 820°C to 890°C at 200W DC power. This also improved the crystalline morphology.

(3) Reference: *“Low temperature rhombohedral single crystal SiGe epitaxy on c-plane sapphire”*, A. J. Duzik et al., *SPIE proceeding volume 9802, Nanosensors, Biosensors, and Info-Tech Sensors and System, 98020D, (2016)*

A new model showed that both pure Ge and SiGe can form single crystal films at the 450-550°C substrate temperature based on thermal expansion calculations. Single crystal Si_{0.15}Ge_{0.85} was grown at a 500°C substrate temperature and 600W DC power of the Si and Ge source target. However, the final stage film did not show a continuous film, instead forming island morphology.

(4) Reference: *“Lattice-alignment mechanism of SiGe on Sapphire”*, Hyun Jung Kim et al., *Acta Materailia, accepted (2017)*

After the atomic layers of the unstrained Si-rich SiGe form on the sapphire interface, the Ge concentration increases modestly and the unstrained form of cubic structures turns into a strained structure up to the Ge concentration uniform. Finally, the lattice spacing distance of Si_{0.15}Ge_{0.85} reaches normal level and the strain is relaxed.

(5) Summary from the previous work

Parameters	Critical values of the parameters	Contribution of the values	Role of the values on twin of film	Role of the values on morphology of film
Source target power (W)	200	High deposition rate (increase flux density)	Rotation (Twin : Single)	Single Crystal
Substrate Temperature (°C)	850	Ge melt	Growth speed (Perpendicular : Horizontal)	Continuous film

Zinc-blende or cubic structure of materials like Si and Ge cannot be structurally settled as a regular formation of crystal on the trigonal structure of sapphire substrate due to lattice constants mismatch. Forming SiGe with twins on the sapphire substrate is normal. Nevertheless, we growth nearly single crystal Si_{0.15}Ge_{0.85} on sapphire from the heteroepitaxy framework.

The clean sapphire substrate without native oxide layer and the first Si-rich layer of SiGe film align to the O-terminated Al₂O₃ substrate, which is the first step for Si_{0.15}Ge_{0.85} film growth. After that, structure deformation of SiGe from cubic to strain structure is crucial for a successful formation of heteroepitaxy. Single crystal growth of epitaxy materials requires a certain amount of energy that triggers a deformation process of the shape of cubic and zinc-blende structure into a strained structure which then aligns the deformed structures on the Si-O bonded layers for SiGe formation, especially for high Ge concentration SiGe film.

Based on the data analysis of the previous work of the team at NASA LaRC / NIA, the (i) substrate temperature must be higher than 850°C for Ge melt and (ii) magnetron DC power must be higher than 200W for a high deposition rate. From these facts out of the previous research, (ii) molten Ge along with the (ii) high deposition rate (flux density) of Ge are important parameters for uniform / continuous single crystal Si_{0.15}Ge_{0.85} film growth.

The previous work generated the following question: [Can we grow uniform single crystal Si_{0.15}Ge_{0.85} film at 500°C if we melt the Ge target before it reaches the substrate with a high deposition rate? If so, which deposition system can be used to melt the target for high flux density?](#) This paper highlights a new method, Molten Target Sputtering (MTS) which melts the Ge target with a high deposition rate at 500°C substrate temperature. The MTS method resulted in the growth of Si_{0.15}Ge_{0.85} film.

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