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Thermoelectric power factor performance of silicon-germanium alloy doped with phosphorus prepared by spark plasma assisted transient liquid phase sintering

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ABSTRACT

This work reports on the successful attempt towards the swift synthesis of Silicon-Germanium (SiGe) alloy doped with phosphorus through spark plasma assisted transient liquid phase sintering. This proposed synthesis of homogeneous SiGe alloy warrants the very shorter duration (17 min.) as opposed to the conventional liquid and solid state synthesis methods which require several hours. SiGe alloys portray the ultra-fine grain features with an excellent relative density > 97%. SiGe alloy with $P_{2.0}$ at.% exhibits n-type semiconducting behavior with the superior thermoelectric power factor of 21.87 μW/cm-K^2 at 750 °C. SiGe alloy reveals the bench marked Vickers hardness of 848 ± 27 $HV_{0.3}$.

Around the globe, the energy crisis and its associated environmental pollution and greenhouse effect create an alarm and trigger the research towards finding out an alternative, sustainable and renewable energy resources for future needs [1,2]. The energy harvesting from waste heat into electricity based on thermoelectricity technology using thermoelectric (TE) materials are being found promising and potential method [3]. It is due to its several merits including robustness, simplicity, long life time, cheaper cost, no moving parts, operation at large power density, noiseless operation, eco-friendly, free from fueling, maintenance etc. [4]. Earlier researchers have been demonstrated significant results for metals and semi-metals for TE applications. Bismuth telluride and lead telluride are implemented successfully in commercial applications. But, these materials have been limited only in low temperature functional applications [5]. Since 1960s, TE couple made of Silicon-Germanium (SiGe) alloys has been used as radioisotope thermoelectric generators (RTGs) to convert radioisotope heat energy into electricity in numerous planetary exploration missions [6]. SiGe alloys have received significant attraction in electricity generation at high temperature (>1000 °C) applications. Other than thermoelectrics, the higher importance is continuing towards SiGe alloys for an advanced and niche commercial application such as solar cells, microelectronics etc. [7,8]. Of any TE materials, the conversion efficiency is denoted by the dimensionless parameter called figure of merit $ZT = S^2\sigma / kT$ [9]. Where, S is the Seebeck coefficient, σ is the electrical conductivity and *k* is the thermal conductivity contributed by lattice waves (phonons) and charge carriers. In order to improve the ZT, the higher power factor ($S^2\sigma$) and lower thermal conductivity are required. In this context, several tailoring approaches such as elemental doping, nano-structuring, energy filtering, resonant energy and second phase nano inclusions are being exercised to reduce the *k* with no significant changes in σ to achieve higher ZT [10]. Thus it may eventually be the heading for an important breakthrough in real time commercialization. Notably, few reports emphasis on the improvement of physical properties of TE materials to withstand the significant load and stress in service conditions to avoid catastrophic failures [11,12]. This can be attained by suitable compositional and grain scale tailoring of TE materials. SiGe alloys are being synthesized by several processing methods such as liquid metallurgy or mechanical alloying (MA) followed by the consolidation using hot isostatic pressing or spark plasma sintering (SPS). In liquid metallurgy, there is dendrite segregation due to the wide separation of the solidus-liquidus region in the SiGe phase [13]. Alternatively, synthesis of SiGe through MA process is being the contemporary method, but prolong processing time leads towards the contamination and oxidation along with the primary SiGe phase [14,15]. Therefore, phase purity and structural homogeneity are the primary hurdles misleading towards the inferior and deleterious TE properties.

The present work reports on spark plasma assisted transient liquid phase sintering of SiGe alloy doped with phosphorus (P). The demonstrated method is found to be a rapid and an effective method to

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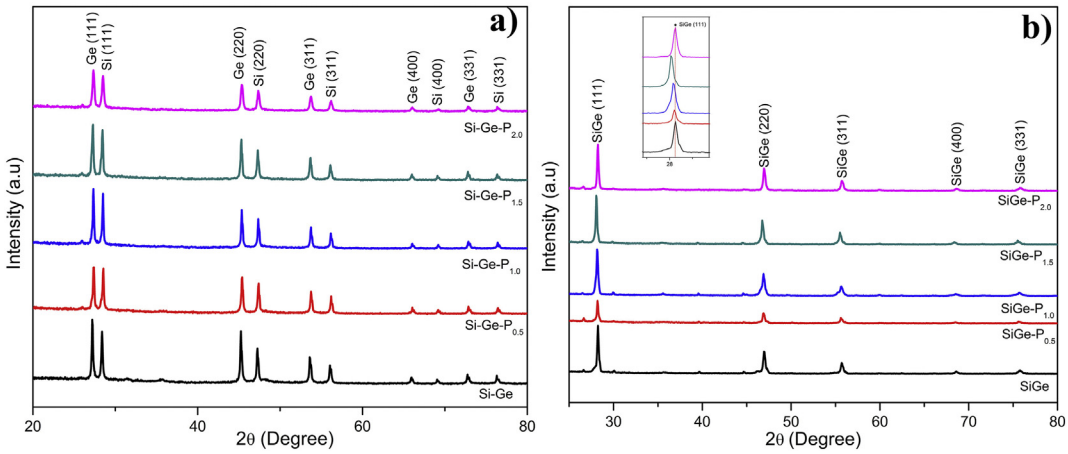

Fig. 1. XRD patterns of (a) 10 h ball milled Si-Ge powder mixture and (b) bulk SiGe alloy (Inset: shift in principal plane (111) of SiGe).

synthesize SiGe alloy with superior chemical homogeneity and desirable power factor performance.

Silicon (Si) (Purity: 99.50%) and germanium (Ge) (Purity: >99.99%) powders were taken in an atomic stoichiometric ratio of 80:20. Phosphorus (P) powder of 99.9% purity taken as doping at the range of 0.5–2 at.%. The manipulation of powders was made inside the glove box in high purity argon (99.999%) to avoid oxidation and contamination. The powders were milled in a high energy planetary ball mill (Fritsch Pulverisette, Germany) in toluene medium at 300 rpm for 10 h. Tungsten carbide vials and the balls were used for ball milling. The ball to powder ratio was maintained as 15:1. The milled powder mixture was reactively alloyed and simultaneously densified at 1150 °C with the applied pressure of 40 MPa using SPS (Dr. Sinter, Japan) in the vacuum pressure > 10 Pa. Structural characterization of Si-Ge milled powder and sintered SiGe alloy were done using high-resolution transmission electron microscope (JEM-2100, JEOL Electron Microscope, Japan) and X-ray diffractometer (ULTIMA-III, Riagaku, Japan) with CuKα radiation (λ = 1.54056 Å). Williamson and Hall relation was used to estimate crystallite size and strain of milled powders and sintered bulk SiGe alloy [16]. The elemental quantification of sintered bulk SiGe alloy was determined using energy dispersive spectroscopy (EDS) (Ultradry, Thermofisher, USA). The relative density of bulk SiGe alloy was determined by Archimedes principle using density measurement kit (AY220, Shimadzu, Japan). Micro-hardness indentation test was conducted on the sintered SiGe alloys using Vickers hardness tester (Vickers 402MD, Wilson hardness, China) for the applied load of 0.300 kg with the dwelling period of 10 s.

Thermoelectric properties of bulk SiGe alloy such as Seebeck coefficient (S), electrical conductivity (σ) and the power factor ($S^2\sigma$) were investigated from RT to 750 °C using LSR-3, Seebeck, Linseis, Germany in the high purity helium (99.999%) atmosphere.

XRD patterns of 10 h milled Si-Ge powders with varying P atomic concentrations and sintered Si(Ge) alloy at 1150 °C is shown in Fig. 1. Si-Ge powder milled for 10 h does not result in alloying which is confirmed by the presence of distinct peaks corresponding to Si and Ge (Fig. 1a). However, it favors in achieving the crystallite size reduction and an intimate mixing of Si-Ge powder. The crystallite size and lattice strain of the milled powder are summarized in Table 1. XRD patterns of post sintered samples confirm the reactive SiGe alloying (Fig. 1b). It is seen that the SPS temperature plays an influential role in the evolution of SiGe solid solution with P doping and simultaneous densification. The effect of SPS processing parameters and mechanism involved in SiGe alloying and densification kinetics was reported elsewhere [17]. The sintered SiGe alloy provides the lattice parameter of 5.4726 Å with the diamond cubic structure of space group Fd-3 m. The estimated 'a' value of SiGe alloy is in concurrence with the JCPDS source and the value reported in the literature [18,19]. It is noticed that there are significant crystallographic defects such as lattice strain and dislocation. In order to justify it more clearly, an enlarged view of the principal plane (111) of Si(Ge) at 2θ position of ~28° is shown in the inset of Fig. 1b. It reveals the shift of peak towards left due to lattice strain indicating the doping of P. The corresponding variation in '**a**' value due to P doping is tabulated in Table 1.

TEM micrograph (Fig. 2a) reveals the nano-crystalline Si-Ge powder mixture obtained by ball milling (10 h). Selective area electron diffraction (SAED) image of Si-Ge powder mixture exhibits the poly nano-crystalline rings of the planes with whiter spots such as (111), (220) and (311) that correspond to major Si phase. Sintered SiGe alloy exhibits uniform ultra-fine grains with the average size of less than ~500 ± 31 nm (Fig. 2b). The elemental mapping of SiGe-$P_{2.0}$ at.% confirms the uniform distribution of constituent elements such as Si, Ge and P (Fig. 2c).

During spark plasma assisted transient liquid phase sintering, the temperature and pressure provide the key contribution towards the in-situ alloying and simultaneous densification of Si-Ge powders doped with P. Fig. 3a and b exhibits an instantaneous densification rate and relative density respectively during SPS of Si-Ge powder mixture. The initial density of Si-Ge powder mixture varies in the range of 56 to 66% with varying P doping concentration. Initially, the rise in SPS temperature from RT to 650 °C does not provide any thermodynamical kinetics between Si and Ge powders which could be evidently observed as stable straight lines (Fig. 3a). Perhaps, only the smaller fraction (~3–4%) of densification occurs at this temperature range which is attributed by an

Table 1
Crystallographic quantification of milled Si-Ge mixture and sintered SiGe alloy.

P (at. %)	Ball milled Si-Ge mixture		Spark plasma sintered SiGe alloy			
	Crystallite Size (nm)	Lattice Strain (%)	Crystallite Size (nm)	Lattice Strain(%)	Lattice parameter(Å)	Hardness($HV_{0.3}$)
0.0	35 ± 4	0.0026	40 ± 5	0.2230	5.4726	848 ± 27
0.5	71 ± 7	0.0009	188 ± 13	0.0022	5.4799	689 ± 22
1.0	87 ± 9	0.0005	197 ± 16	0.0025	5.4798	652 ± 13
1.5	44 ± 6	0.0003	240 ± 22	0.0032	5.4954	592 ± 24
2.0	35 ± 5	0.0004	210 ± 19	0.0023	5.4713	589 ± 22