A review on Silicide based materials for thermoelectric applications

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Abstract— Thermoelectric materials are considered prime in converting energy, thanks to its nature to translate heat into electricity openly. Low efficiency and the intricacy in fabrication restrict their applications commercially. Moreover, there are certain thermoelectric materials such as alloys of telluride owing to their toxicity present peril to the environment. There is scarcity in present examination to get an ecological gracious thermoelectric material which is available in abundance to be utilized in large volumes owing to the low efficiency. The paper presents a review of such thermoelectric material which is ecological gracious. In the beginning, a number of techniques employed in advancing the figure of merit (ZT) is offered, then an in - depth review of several thermoelectric materials which are silicon-based is showed. N-type doping of Mg2Si0.75Sn0.25 among aluminum along with lead at operational temperature of 850 K scaled up the value of ZT by a factor of 2. Considerable addition in carrier concentration resulted in the attainment of figure of merit with peak value of 1.4. Techniques such as nanostructuring and doping have boosted silicides such as HMS to show a remarkable achievement in the attainment of dimensionless figure of merit. Iron disilicide (FeSi2), Chromium silicide (CrSi2) and Cobalt Silicide (CoSi) have shown their worth to be employed as thermoelectric materials in industries in near future. It is also recommended to analyze supplementary types of metal oxides and organic materials which exhibit thermoelectric traits.

I. INTRODUCTION

As the density of the electronic devices is increasing owing to the contraction in the dimensions of components, scientists and engineers are facing an immense challenge in controlling the dissipation of heat in present devices. This leads to the necessity of thermal management right from the beginning of any design procedure. Thin films made of thermoelectric materials have been accepted recently as a vital division of energy materials responsible in converting waste heat into electrical energy. It has opened the doors to possibly and successfully scale down the dimensions of thermoelectric devices to nano scale with performance analogous to bulk materials. Further, materials of nano-scale are expected to demonstrate exceptional thermoelectric performance over bulk materials. The reason for this is because of the effect of low dimensional quantum size. Hence it is imperative in exploring and developing right category of materials to be employed in manufacturing thermal interface devices with elevated thermal conductivity.

In current scenario, lower utilization of thermoelectric devices is owing to their comparatively high expenditure

and low efficiency. The scarcity of energy and global warming stands as a gigantic problem which has ultimately attracted the issues of energy preserving and diminution of carbon emission. For any thermoelectric material, the translation efficiency is linked to ZT. Figure of merit (ZT) is expressed in Eq. (1) as [1]

$$ZT = \frac{S^2}{\rho k} T = \frac{S^2}{\rho (K_e + K_l)} T \qquad (1)$$

Here S stands for Seebeck coefficient whereas ρ stands for electrical resistivity. Thermal conductivity is shown by κ. Thermal conductivity defines ability of transfer of heat through a material. Equation 1 clarifies that for attaining high value of ZT, thermal conductivity must be kept low. Thermal conductivity holds two components, electrical thermal conductivity along with lattice thermal conductivity denoted by K_e and K_l respectively. For this reason, decrease in thermal conductivity will also result in low the electrical conductivity as well. A method to beat this is by employing phonon scattering [2].

II.   IMPORTANCE OF THIN FILMS

In the previous decade or so, the deposition of thin film has emerged an exceedingly valuable technology which has seeped in every foremost industry. Thin films are nothing but materials of thin layers whose thickness varies from nanometers to micrometers. Thin film technology is used in manufacturing thin film batteries, photo cells and solar cells etc. Thin films are predominantly used in industries such as aerospace and machine tool. The likelihood of fine-tuning of firmness and inertness of thin films guards the materials against both corrosion and oxidation. This in return stretches the longevity of objects significantly.

As per the reports of Hicks and Dresselhaus, the efficiency of materials with low dimensions is far better than bulk. Such nanostructured thermoelectric material with lower dimensions contributes in enlarged density of states of Fermi level and improvement in phonon scattering. Since it is known that sintering blocks is quite tedious to attain the miniaturization of the thermoelectric devices, therefore a large number of deposition techniques have been employed to acquire the thermoelectric thin films to name a few like IBS, MBE, MOCVD and electrochemical deposition. For conducting thin films, it is desirable that atomic structure of thin films to be amorphous with spatial homogeneity to be in nanoscale for device compatibility. This can be seen in super conducting nanowire single photon detectors (SNSPD)

[3]. A classic means to craft amorphous thin films is through sputtering the cooled surfaces [4]. The technique of bombardment of the sample with ions using a focused ion beam can be given nearby by means of nanometer scale spatial resolution to tune normal state resistivity. Narrow weak spots are fashioned when the limit of dose is large demonstrated among cuprites [5] along with niobium nitride [6].

III.   Enhancing figure of merit in thermoelectricity

It is clear from equation (1), those materials which exhibit large values of ZT possesses enhanced seebeck coefficient along with better electrical conductivity, simultaneously keeping lower values of thermal conductivity. For a thermoelectric material electrical conductivity σ is given as:

$$\sigma = \frac{1}{\rho} \eta e \mu \qquad (2)$$

Where η is the concentration of carriers and μ represents the mobility of carrier. Electrical conductivity can be improved by accumulating chemical dopants. The mobility of charge carrier's will shrink by doping as scattering amid charge carriers and dopants rises. In addition, the density of charge carriers gets augmented due to the availability of extra valence electron in each dopant. So for achieving explicit larger Seebeck coefficient, only one type of carrier remains. The doping polarities of carriers influences the carriers to persistently remain at cool region while other to reverse the effect of seebeck.

To apprehend higher values of ZT, an efficient thermoelectric material must own low values of thermal conductivity. In order to decrease thermal conductivity, scattering of phonon ought to be increased. In a thermoelectric material, the subsequent heat transport by travelling of phonons through crystal lattice [7, 8] leads to thermal conductivity. Equation 3 shows the relationship as

$$k_{tot} = k_e + k_L \qquad (3)$$

Electron thermal conductivity as per Weidemann-Franz Law [9] is given away in equation (4)

$$k_e = L \sigma T \qquad (4)$$

Here L represents Lorenz number. From equation 4, it is evident that dipping k_e is not forever a dependable option because the electrical conductivity gets affected which halts the progress in the value of ZT. Thermoelectric materials which are made of semiconductors, bulk portion of thermal conductivity are contributed by lattice thermal conductivity.

3.1 The optimal Seebeck coefficient

In this day and age, efficient thermoelectric materials are customarily semiconductors where by doping acceptor or donor impurities, the concentration of the carriers can be regulated. The impurities decide the polarity of the Seebeck coefficient. Minority carriers diminish the scale of the Seebeck coefficient in addition augments the thermal conductivity all the way through bipolar conduction. In the presence of single polarity carriers, the extent of the Seebeck coefficient increases as the concentration of carrier reduces. The probability of seebeck coefficient scales the order of ± 1000 µV/K or even more in larger energy gap. The Seebeck coefficient which facilitates the maximum power factor is nearer to that which provides the maximum figure of merit. It is obvious when the electronic contribution is taken in consideration to thermal conductivity. The optimal Seebeck coefficient does not vary greatly from one material to another. The concentration of carrier intended for a specified Seebeck coefficient rely on effective mass. Higher Seebeck coefficient is often present where carrier concentration is low. Those metals whose carrier concentration is on higher side, attracts higher values of electrical conductivity and poorer Seebeck coefficient [9] values. Review of thermoelectric properties at 300 K is given in table 1.

Table 1: Review of thermoelectric properties at 300 K.

TE property	Insulators	Semiconductors	Metals
Carrier concentration	Low	Low	High
Seebeck Coefficient	1000 µV / K	0-3 µV / K	200-300 µV / K
Electrical conductivity	$< 10^{-6}$ $(\Omega.m)^{-1}$	$10^{-6} < \sigma < 10^{5}$ $(\Omega.m)^{-1}$	$> 10^{5}$ $(\Omega.m)^{-1}$

IV. ADVANCES IN ECOLOGICAL GRACIOUS THERMOELECTRIC MATERIALS

Numerous thermoelectric materials that were found with high values of ZT but majority of those efficient thermoelectric materials holds toxicity as well as are ecological ungracious. Silicides and oxides consistent with He, Liu et al [10], are regarded eco-gracious thermoelectric resources owing to less contamination with huge measures within the environment. During this review, scope is merely to silicon-based thermoelectric materials only.

4.1 Thermoelectric materials (Silicon-based)

Silicon is the most familiar and extensively used semiconductors in industries thanks to its ecological gracious, economical and abundance in nature [11, 12]. Owing to large thermal conductivity at 300K, silicon is understood meager having ZT value of 0.01 at 300 K [13]. Nanotechnology eliminates this demerit by reducing the size of the grain. In current time, the dynamic progress in low dimensionality tactic has revealed thrilling effect in enriching ZT and limiting k in silicon based materials alongside restraining capacity of the material jointly amid highly developed IC techniques crafting it further suitable from unrefined materials to realistic integration. Since Si is an excellent semiconductor material, in recent times, numerous bright writings about it's material prospectus is projected. Narducci, et al. [14] in 2015 proposed the utility of nano-precipitates within thermoelectric performance of silicon based bulk as well as films. Nozariasbmarz, et al. [15] concluded that bulk metal silicide thermoelectric materials in depth till 2017. Gadea, et al. [16] in 2018 did the review of superior microstructure silicon based thermoelectric material to put forward application leaning outlook. Nakamura [17] deeply illustrated vivid diminution of *k* in the accurate scheming of a silicon base epitaxy.

In 2019, He, et al. [18] orderly reviewed the thermoelectric behavior in relation to the nano bulk structure of silicon along with alloys of SiGe. Furthermore, thermoelectric traits of Si fragment cultivated from wafer production were introduced. Tanusilp and Kurosaki [19] in a few words did the review of silicon base thermoelectric materials along its synthesis by the technique of nano-structuring. Hochbaum, et al [20] showed diminish in lattice thermal conductivity by a factor of 100 in silicon nano-wires. This caused attainment of ZT value to be 0.6 at 300K. The fall of lattice thermal conductivity of nano structured silicon is because of sturdy scattering of phonon.

Bux and Blair, et al [21] in 2009 showed a ZT value equals to 0.7 at operating temperature 1275 K for nano-structured bulk Si with n-type polarity by sinking thermal conductivity and degrading electron mobility. A fall of 90% k_L was observed due to scattering of interfacial phonon. Yang et al [22] proposed that the value of k_L in silicon nanocomposites gets minimized as a result of rising phonon scattering. Further reports proposed incredibly small k_L (< 0.1 W/mK) at operating temperature 300 K exhibited by nano-porous silicon.

In 2011, Yang and Li [23] utilized nano thermodynamics representation to compute lattice thermal conductivity of nano-porous, nano-crystalline along with nano-structured bulk Si. They found that, nano-porous silicon display lesser k_L in contrast to silicon nano-wires. Nielsch and

Bachmann, et al [24] forwarded nano-structured silicon a promising substitute intended for high- effectiveness within the thermoelectric applications. Further it was noted that by doping of germanium or manganese, the efficiency of Si nanostructures was improved.

4.2 Thermoelectric materials (Mg2Si)

Mg2Si- oriented thermoelectric materials are promising within 500 to 900 K. This is because of immense attainment in the values of ZT to 1.3 [25, 26, 27]. Because of the extreme closeness in the boiling value of magnesium and the melting value of Mg2Si, treatment of Mg2Si is not easy [28]. Method like spark plasma and ball-milling are therefore employed to synthesize Mg2Si. Bux, et al [25] in 2011 performed the doping of Mg2Si with Bismuth.   Synthesis was achieved by mechano chemical method. ZT = 0.7 was reported at temperature 775 K. This increase in ZT resulted by noteworthy drop within the lattice thermal conductivity.

Fusion techniques used were not capable to adjust the composition and feat of silicide owing to the oxidation and volatilization. Spark plasma is employed into nearly all studies at low temperature owing to the exceedingly large diffusion velocity. This is to avoid the oxidation of Mg [29]. SPS method was utilized by Hu, Mayson and Barnett [30] in order to synthesize Mg2Si with aluminum as dopant at 750ºC. Maximum value of ZT was reported as 0.58 at temperature 844 K.

Hu, et al reported the likelihood of upper electrical conductivity is obtained due to full densification of Mg2Si in spark plasma. Tani and Kido [31] performed the doping of the silicide and phosphorus at (300-900K). The outcome was the value of ZT to 0.33 at 865K. Yang, et al [27] utilized the technique of SPS for synthesizing the Bi-doped Mg2Si powders. This nano-composite structure trims down conductivity and augment the seebeck coefficient. Taken as a whole, thermoelectric performance improves and a max ZT=0.8 (nearly 63% higher than silicide with no nanocomposite structure) is achieved at temperature 823 K.

4.3 Thermoelectric materials (SiGe)

For elevated temperature applications, silicon germanium (SiGe) is well thought-out a big thermoelectric material. With lower values of vapour pressure, it also offers superior resistance against atmospheric oxidation. For high temperatures (~1173 K) applications such as power generation, SiGe is presently the premium thermoelectric material. For p-type nanostructured bulk Si80Ge20, Joshi, et al [32] achieved value of ZT to be of 0.95 at 800°C -900ºC with boron doping. As per Joshi et al, the

various augmentations in the value of ZT are due to noteworthy diminution of thermal conductivity. In 2009, Zhu, et al [33] showed the value of ZT to be around 0.94 at operating temperature of 900°C. The enhancement of boundary phonon scattering resulted from drop in thermal conductivity. The small quantity of Germanium significantly reduces the total cost of fabrication cost. Modulation doping approach is one more mode to realize high value of ZT in SiGe nanocomposites. As per Yu and Chen, et al [34], doping methodology can be further enhanced by employing a skinny spacer film which ultimately improves measured performance.

In correlation to trial approach, various investigations on properties of SiGe have undergone by numerous researchers. The thermoelectric properties of nanoporous SiGe was obtained by Lee, et al [35] in 2012. In single SiGe nanowires, the ZT value was predicted to 2.2 at temperature 800 K and nearly 0.46 at temperature 450 K. An improved model was projected by Yi and Yu [36]. The thermoelectric traits of highly doped SiGe nano-wires were predicted at various temperature ranges. The obtained result recommends the value of ZT to be 1.9, 1.5, 1.2 and 0.8 is yield at temperature 800 K, temperature 600 K, temperature 450 K and temperature 300 K respectively.

4.4 Thermoelectric materials (High manganese)

Higher manganese silicide (HMS) is known for it's composition exceeding the amounts of Si with Mn [37]. HMS is represented by five phases. These phases have analogous properties. The structure is tetragonal crystal structure. The energy gap varies from 0.4-0.7 eV. The thermal conductivity of HMS exhibits lower values. ZT was reported nearly 0.4 at temperature 800 K in a non-doped HMS [38]. Girard, et al [39] in 2014 achieved advancement in the value of ZT to 0.52 ± 0.08 at operating temperature 750 K in an un-doped crystal of HMS. Itoh and Yamada [40] presented mechanical alloying of MnSi1.73 to achieve maximum value of ZT of 0.47 at temperature 873 K. Numerous experiments have been attempted on polycrystalline HMS to attain growth in thermoelectric characteristics. Polycrystalline HMS were synthesized by SPS by An and Choi, at temperature 1123 K. The maximum value of ZT to be 0.41 was obtained. Luo, et al [41] in 2011 obtained maximum value of ZT to 0.65 at operating temperature 850 K. This was possible due to the doping of HMS with Aluminum.

As per Luo et al, the development in the value of ZT was mainly due to the addition of Al in HMS. It leads to rise in the electrical conductivity and fall in thermal conductivity. As per Ikuto et al [42], the improvement in the thermoelectric properties was due to the doping of HMS with aluminum. Al doping lowers the thermal

conductivity. Aoyama, et al [43] in 2005 set up that by accumulation of Ge into HMS, there is early boost in the volume concentration of MnSi. Zhou, et al [44] in 2009 employed induction melting and hot-pressing for doping polycrystalline HMS among Ge thereby obtaining ZT =0.6 at 833 K.

4.5 Thermoelectric materials (FeSi2)

Thermoelectric devices whose applications falls in temperature range between 230 ^{0} C – 630 ^{0} C, iron silicide shows immense possibility in driving instrument. β- FeSi2 has been distantly acknowledged in thermal sensing applications and also in the fields of optoelectronics. A range of experiment has been conducted to get better thermoelectric performances of β-FeSi2. Ware and McNeill in 1964 obtained β- FeSi2 of n-type by doping β- FeSi2 with cobalt. Doping β- FeSi2 with cobalt was also achieved by an experiment conducted in 2002 by Ur and Kim, et al [45] through mechanical alloying. It was observed that finer grain size is obtained by mechanical alloying materials which ultimately reduced the lattice thermal conductivity thereby obtained improvement in thermoelectric efficiency.

Kim, et al [46] in 2003 prepared β- FeSi2 by the technique of powder metallurgy. It was observed that co-doping with Chromium, Cobalt and Germanium enhanced the ZT value to 1.3 x 10-4 K-1 at temperature 845 K. FeSi2 has shown highest ZT = 0.4 in β- FeSi2 of n-type and ZT=0.25 in β-FeSi2 of p-type.

4.6 Thermoelectric materials (CrSi2)

Using density functional theory Pandey and Singh [47] showed that the thermoelectric properties of doped CrSi2 can be managed by defect transition levels from dopants. It was also noticed that the accumulation of doping aluminum or manganese in CrSi2 augments in thermopower and further reported that n-type attain higher thermopower in comparison to the p-type doped CrSi2. CrSi2 exhibits good electrical conductivity and thermopower. It has large thermal conductivity. Highest ZT value is presented to be 0.2 - 0.25 at 600 ℃ in un-doped CrSi2 [48]. A quite a lot of researches have revealed that the thermoelectric properties improve appreciably by doping.

Perumal, et al [49] in 2013 formed the CrSi2-x composites (where 0< x< 0.1) by varying temperature from 300K toward 800K. It was established that a significant reduction in the value of Seeback coefficient along with electrical resistivity at x > 0.04. The peak value of ZT= 0.1 is noticed at temperature 650 K. Several attempts were made to replace manganese and aluminum by polycrystalline CrSi2 by utilizing the technique of arc melting as well as hot pressing [50]. It was evident that lattice values escalated by the contents of Manganese as well as Aluminum. Perumal, et al [51] suggested numerous ways in the processing of CrSi2 as (i) forming precipitate by means of solid state phase transformation, (ii) speedy solidification through the technique of melt-spinning, (iii) employing the technique of mechanical alloying. Kajikawa, et al [52] collectively applied both SPS as well as hot pressing in processing CrSi2 at temperature 1573 K. Further approaches like solo crystal CrSi2 nanowires were explored to check their effect in enhancing ZT in upcoming thermoelectric areas [53].

4.7 Thermoelectric materials (Ru2Si3)

The thermal stability of ruthenium silicide is high. It's resistance to chemical exposure is also high. This makes the material well suited for application where the requirement of operational temperature is very high such as space applications. C.B Vining grew an un-doped single crystal of ruthenium Silicide for theoretical analysis. Attainment of higher value of figure of merit by Ru2Si3 was possible in comparison to current state-of-art SiGe as per Vining's report. Further ahead, Vining and Allevato also reported the role of addition of p-type Ru2Si3 in improving the value of figure of merit to a scale of 3 and in contrast to current SiGe standard; n-type Ru2Si3 displayed 50% better results. Ivanenko, et al in 2003, using the technique of floating zone was successful in doping single crystal Ru2Si3 with Manganese. The outcomes reported the effect of doping on the electrical resistivity. Mn-doped Ru2Si3 was found to have much lower electrical resistivity in comparison to the un-doped crystal. It an increase by scale of 2 was noted in the mobility of carrier in Mn-doped Ru2Si3 as compared to undoped Ru2Si3.

Table 2: Thermoelectric properties of un-doped and Mn-doped single crystal of Ru2Si3.

Thermoelectric properties	Mn-doping	Without doping	Observations
Electrical Resistivity	15 Ω	22 Ω	Mobility of carrier increases
Seebeck Coefficient at 500 K.	400 µV / K	300 µV / K	Samples without doping showed negative seebeck value in whereas samples with Mn doping showed positive seebeck value.
Thermal conductivity	5 W/ K m	5 W/ K m	Thermal conductivity is same at 300 K in both samples but doped sample below 100 K is much high than other.
Figure of Merit	0.3	0.2	Mn-doping displayed high ZT.

In 2004, Ivanenko et al [54] reported that higher values of Seeback coefficient are possible by doping pure Mn with Ru_2Si_3 in comparison to the un-doped Ru_2Si_3 at 300 K. The (ZT) value at working temperature of 800 K in Mn-doped Ru_2Si_3 is calculated to be 0.2 and 0.27 for un-doped. Krivosheev et al [55] by the technique of zone arc melting in combination with optical heating successfully doped Ru_2Si_3 with manganese. The thermoelectric properties exhibited by the experiment are illustrated in Table 2.

4.8 Thermoelectric materials (Mo-Si) based TE

Molybdenum silicide ($MoSi_2$) in recent times has acknowledged substantial interest for thermoelectric applications at high temperature. $MoSi_2$ exhibits high melting point. It also displays higher resistance to oxidation which attracts $MoSi_2$ as a heating element for the reason that it can endure extended exposure to air. For heating application, it becomes obvious to comprehend the thermal and mechanical traits of $MoSi_2$ since these traits are fundamental in designing. The mainstream research done till has focused in oxidizing and synthesizing α-MoSi2.

As per reports of Krontiras et al., the value of electrical resistivity at operational temperature 300 K was $0.063 \ 10^{-3}$ Ω cm. Vries, et al presented electrical resistivity at temperature 300 K to be $0.06 \ 10^{-3}$ Ω cm whereas Yamada, et al [56] presented $0.75 \ 10^{-3}$ Ω cm of electric resistivity. We can observe a great disagreement in the value of thermal conductivity put forward by Takami, et al, as compared to report by groups. Using a COMSOL simulation program, Takami et al. used the value of thermal conductivity to be 44.1 W/m.K [57] whereas other researchers employed roughly 60 W/m.K at 300 K. Y. Ohishi, et al [58] reports from the powder XRD patterns that the occurrence of peaks in MoSi2 matches with α- MoSi2. The matching indicates that the powder employed initially was clean α- MoSi2. It is very noteworthy that the XRD pattern reported the occurrence of small peaks at an angle of 38°C and 41°C in Pre and Post SPS. The observed peak positions are similar with that of Mo5Si3. N-type Si nanoparticles were used to fabricate mass Si nanocrystal by sintering process by K. Kurosaki, et al [59]. The thermoelectric properties of mass silicon were presented. Silane gas via a vapor-phase synthetic route was used for synthesis. The report suggested the value of ZT to 0.5 at temperature 1223 K.

V. RESULTS AND DISCUSSION

Hochbaum, et al showed diminish in lattice thermal conductivity by a factor of 100 in silicon nano-wires. This caused attainment of ZT value to be 0.6 at temperature 300K. The fall of lattice thermal conductivity of nano structured silicon is because of sturdy scattering of phonon. Bux and Blair, et al showed a ZT value equals to 0.7 at operating temperature 1275 K for nano-structured bulk Si with n-type polarity by sinking thermal conductivity and degrading electron mobility. A fall of 90% k_L was observed due to scattering of interfacial phonon.

Yang, et al proposed that the value of k_L in silicon nanocomposites gets minimized as a result of rising phonon scattering. Yang and Li utilized nano thermodynamics representation to compute lattice thermal conductivity of nano-porous, nano-crystalline and nano-structured bulk Si. They found that, nano-porous silicon display lesser k_L in contrast to silicon nano-wires. Nielsch and Bachmann, et al forwarded nano-structured silicon a promising substitute intended for high- effectiveness within the thermoelectric applications. Further it was noted that by doping of germanium or manganese, the efficiency of Si nanostructures was improved

significantly. Bux et al performed the doping of Mg_2Si with Bismuth.   Synthesis was achieved by mechano chemical method. The value of ZT was reported to be 0.7 at temperature 775 K.

SPS method was utilized by Hu, Mayson and Barnett in order to synthesize Mg_2Si with aluminum as dopant at 750°C. Maximum value of ZT was reported as 0.58 at temperature 844 K. Hu, et al reported the likelihood in upper electrical conductivity due to full densification of Mg_2Si in spark plasma. Tani and Kido performed the doping of the silicide with phosphorus at (300-900K). The outcome was the value of ZT to 0.33 at 865K. For p-type nanostructured bulk $Si_{80}Ge_{20}$, Joshi et al achieved value of ZT to 0.95 at 800°C-900°C with boron doping. Zhu, et al showed the value of ZT to be around 0.94 at operating temperature of 900°C. Yu and Chen et al applied modulation doping approach to realize high value of ZT in SiGe nanocomposites. Lee, et al studied thermoelectric behavior of single SiGe nanowires and predicted the value of ZT to 2.2 at temperature 800 K and value of ZT to be nearly 0.46 at temperature 450 K.

Girard achieved improvement in the value of ZT to 0.52 ± 0.08 at operating temperature 750 K in an un-doped crystal of HMS and. Itoh and Yamada presented mechanical alloying of $MnSi_{1.73}$ to achieve maximum value of ZT of 0.47 at temperature 873 K. An and Choi employed SPS at temperature 1123 K for synthesizing polycrystalline HMS. The highest ZT value of 0.41 was obtained. Luo et al doped HMS with aluminum and obtained maximum value of ZT to 0.65 at operating temperature 850 K. Doping lead to rise in the electrical conductivity and fall in thermal conductivity. Zhou, et al applied induction melting and hot-pressing technique for doping polycrystalline HMS with Germanium. Ur and Kim et al utilized the of process of mechanical alloying and vacuum hot pressing for doping β- $FeSi_2$ with cobalt. It was observed that finer grain size obtained by mechanical alloying of materials. Kim, et al prepared β- $FeSi_2$ by the technique of powder metallurgy. Perumal, et al formed the $CrSi_{2-x}$ composites (where $0 < x < 0.1$) by varying temperature from 300K toward 800K and established a significant reduction in the value of Seeback coefficient along with electrical resistivity at $x > 0.04$. Perumal, et al suggested mechanical alloying technique with ball-milling or Spark Plasma for processing $CrSi_2$. Vining and Allevato reported that addition of p-type Ru_2Si_3 improves figure of merit to a scale of 3.

Ivanenko, et al employed floating zone technique for doping single crystal Ru_2Si_3 with manganese. An increase by scale of 2 was observed in the mobility of

carrier in Mn-doped Ru_2Si_3 as compared to undoped Ru2Si3. The value of electrical resistivity was reported by Krontiras et al.at operational temperature 300 K to 0.063 10 3 Ω whereas Vries et al reported 0.06 10^{-3} Ω cm and 0.75 10^{-3} 3 Ω cm by Yamada et al. Y. Ohishi et al reports from the powder XRD patterns that the occurrence of peaks in MoSi2 match with α-MoSi2. The matching indicates that the powder employed initially was clean α-MoSi2. It is very noteworthy that the XRD pattern reported the occurrence of small peaks at an angle of 38°C and 41°C in Pre and Post SPS. The observed peak positions are similar with that of Mo5Si3. N-type Si nanoparticles were used to fabricate mass Si nanocrystal by sintering process by K. Kurosaki et al.

VI.   CONCLUSION

Silicides as thermoelectric materials show potential in industrial applications owing to economical in cost, ecological gracious, availability in ample amount. They moreover facilitates in reaching higher values of figure of merit. Silicides such as Mg_2Si, SiGe and HMS attained high values of ZT in comparison to tellurides such as Bi2Te3 and PbTe. The prospect of obtaining higher values of ZT in silicides can be improved using dopants in single or polycrystalline material and methods such as optimum alloying. CrSi2 which has lower band gap in recent research has shown increase in the prospect of modifying itself to a beneficial thermoelectric substance in commercial applications. Ru2Si3 can be significantly utilized in elevated temperature applications like space power. It can thus be concluded that there is a large room for improvement in the utilization of silicides as thermoelectric material in achieving superior values of figure of merit (ZT). Although certain silicides have obtained superior values of figure of merit, other silicides possess high anisotropic properties which can be utilized significantly in anisotropic areas. Therefore by perceiving deeply the thermoelectric behavior of silicides, further there opens a large room for improvement in thermoelectric performances.

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