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A novel method to synthesize bulk super saturated solid solutions $Ge_{1-x}Sn_x$ ($x \le 5.0\%$)

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Sn substituted $Ge_{1-x}Sn_x$ type phases can have a variety of optoelectronic and energy applications as the band gap in these materials is tunable by varying x. Super saturated solid solutions $Ge_{1-x}Sn_x$ ($x \le 5.0\%$) have been synthesized by ball milling the elements Ca, Ge and Sn together for a period of 6 h. Extended ball milling beyond 6 h has only a marginal effect on the incorporation of Sn in Ge. By treating the ball milled product in concentrated HCl and subsequently washing in distilled water, the impurity phases CaSn and Sn can be washed away. Spark plasma sintering (SPS) at 500 °C for 5 min at a pressure of 350 MPa has yielded discs of 70% theoretical density. However, the amount of Sn incorporated in the spark plasma sintered discs have been reduced to 2.5 at.%. Resistivity and Seebeck coefficient measurements show the semiconducting nature of these samples and the capability of p- and n-type doping with Ga and P, respectively.

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1. Introduction

Among the Group IV elements Si, Ge and Sn, a complete solid solution between only Si and Ge is possible. In contrast, the equilibrium solubility of Sn in Ge is very low - less than 1% [1] - due to large atom size mismatch which is approximately 15%. The issue of low solubility can be overcome by employing non-equilibrium methods which allow the incorporation of as much as 10–25 at. %, depending upon the method employed [2–4]. In amorphous films as much as 40 at. % Sn can be incorporated [5]. Super saturated solid solutions of $Ge_{1-x}Sn_x$ have a wide range of applications as described below.

Like Si and Ge, α-Sn, which is stable below 13.2 °C, crystallizes in the cubic diamond structure. While the high temperature form (β-Sn) is metallic, α-Sn is a semimetal with the energy gap at the Γ point of −0.4 eV. On the other hand Ge is a semiconductor with a direct gap of 0.78 eV at the Γ point and an indirect gap of 0.67 eV between Γ and L points. Hence, a systematic down shift in the band gap is possible in $Ge_{1-x}Sn_x$ alloys with increasing Sn content. In addition, Substitution of Sn allows to achieve indirect to direct band gap (E_g) transition as the Sn content is increased beyond 6.5–11 at.% due to a faster decrease of the gap at the Γ point [6–8]. In a compound $Ge_{0.75}Sn_{0.25}$, the bandgap E_g can be as low as 0.15 eV [7,9]. It has been demonstrated experimentally, particularly on thin films grown by molecular beam epitaxy (MBE) [10,11], chemical vapor transport (CVT) [12], and pulsed laser annealing [13,14] that significant incorporation of Sn is possible without introducing static defects such as dislocations. Due to the high quality achieved in $Ge_{1-x}Sn_x$ films, lasing action and photoluminescence [8,15] have been demonstrated. Alloys of Group IV elements have higher electron and hole mobilities compared to III-V compounds and the band gap is tunable in $Ge_{1-x}Sn_x$ by changing x [16,17]. Hence the growth of $Ge_{1-x}Sn_x$ films on Si-substrates instead of III-V compound semiconductor films for a variety of applications including mid-IR photo detectors [12], and optical interconnects for faster electronic devices, is presently a preferred approach. In addition $Ge_{1-x}Sn_x$ may exhibit the Gunn effect [18].

Apart from thin films, other forms of $Ge_{1-x}Sn_x$ alloys such as quantum dots [19,20] and nanowires [21,22] with higher concentration of Sn have been reported. Particularly, by a wet chemical route, colloidal $Ge_{1-x}Sn_x$ quantum dots (QDs) with an average size of 2 nm with 5.5 at.% < x < 23.6 at.% have been synthesized [19]. Growth of 300–500 nm long and uniform diameter $Ge_{1-x}Sn_x$ nanowires (NWs) with Sn content ~ 9.2 at.% has also been reported [21]. In addition synthesis of amorphous $Ge_{1-x}Sn_x$ is also reported [23–26].

While non-equilibrium methods enable the incorporation of high Sn content in thin films, NWs and QDs, it is not clear how

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much Sn incorporation is possible in bulk $Ge_{1-x}Sn_x$ synthesized using a low temperature route such as high energy ball milling. Because of its high mobility and narrow band gap, bulk $Ge_{1-x}Sn_x$ can find applications in thermoelectric energy harvesting and Peltier cooling.

2. Experiments

Since the equilibrium solubility of Sn in Ge is <1%, a low temperature synthesis route may provide a better approach to incorporate more Sn in Ge. Since mechanical alloying (MA) or high energy ball milling is essentially a low temperature route, it could be a promising method to achieve higher solubility of Sn in Ge. In the mechanical alloying process, constituents are repeatedly cold welded, fractured and re-welded. This process is essentially known to facilitate the synthesis of extended solid solutions [27]. Such non-equilibrium products are otherwise impossible to synthesize.

Motivated by the reports of successful synthesis of many metastable materials [27], we first attempted to synthesize $Ge_{1-x}Sn_x$ extended solution by ball milling elements Ge and Sn together for several hours in a WC vial containing two or more WC balls. We used a ball milling unit (SPEX Sample Prep; model: 8000 M Mixer/Mill) that was capable of vibrating at 1080 cycles/min. After ball milling for an extended period of 12 h, it was found that the powder x-ray diffraction peaks were broadened; however as shown in Fig. 1, no shift in the peak positions was observed suggesting that only negligible amount of Sn was incorporated in the Ge lattice.

Due to the failure of the first method, a second approach which involves the synthesis of $CaGe_{2-x}Sn_x$ by ball mailing was adopted. It has been reported that $CaGe_{2-x}Sn_x$ with Sn content as high as $x = 0.09$ can be synthesized [28]. Such a compound can subsequently be washed with concentrated HCl to remove all the Ca atoms and the resulting compound is $Ge_{1-x}Sn_xH_xOH_{1-x}$. Our hypothesis is to decompose $Ge_{1-x}Sn_xH_{1-x}OH_x$ to obtain $Ge_{1-x}Sn_x$ alloy with higher Sn content. Hence Ca, Ge and Sn in appropriate ratios were ball milled for different durations from 1 h to 22 h. Powder X-ray diffraction (XRD) (Rigaku, MiniFlex II) was recorded to check the phase evolution at different stages. Powder XRD of Ge was also collected and used as a calibration standard.

A Spark Plasma Sintering (SPS) unit (Dr. Sinter Lab, Model: SPS-*211Lx*) was employed to obtain disc samples. In order to dope the sample, either Ga (p-type) or P (n-type) was thoroughly mixed with the powder samples and loaded into a WC die (10 mm dia.). To minimize the Sn precipitation, the samples were pressed for a short duration of 5 min at 500 °C while maintaining a relatively high pressure of 350 MPa. The pressed discs were found to be 70% of theoretical density. While the Porosity is expected to influence the resistivity strongly, the Seebeck coefficient is less sensitive to the low density of the samples.

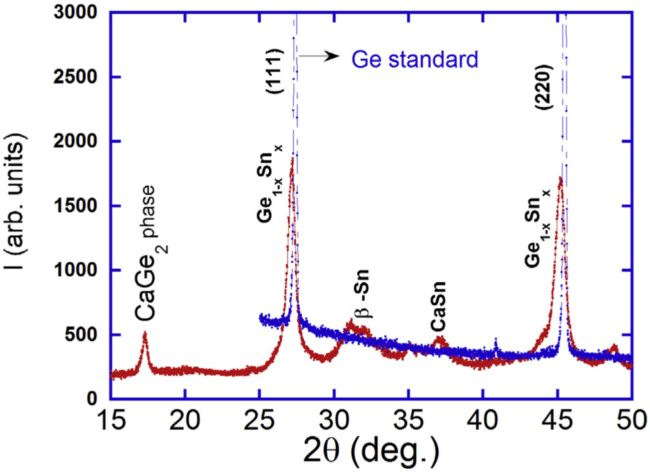

Fig. 2. Powder XRD showing the formation of the phases $CaGe_2$, $Ge_{1-x}Sn_x$ solid solution and CaSn. The unreacted Sn is also marked.

3. Results and discussions

The powder XRD patterns recorded after ball milling for 2 h are given in Fig. 2. As we see, the appearance of a low angle peak ($2\theta \sim 17.4°$) suggests the formation of $CaGe_2$ phase. The remaining minority phases can be identified as CaSn and unreacted Sn. The majority phase is Ge with its peaks not only broadened but also shifted to lower angles suggesting the incorporation of Sn. After prolonged ball milling, as shown in Fig. 3., while $CaGe_2$ phase disappears slowly, the peaks of the Ge (majority phase) shift further to lower 2θ values with CaSn and Sn as minority phases. By using Vegard's law, the estimated amount of Sn incorporated is around 5.0% which is substantially larger than the equilibrium solubility of Sn in Ge. The lattice parameter changes from 5.658 Å to 5.698 Å upon substitution of Sn. The role of $CaGe_2$ phase in the formation of extended solid solution $Ca_{1-x}Sn_x$ is not clear. However, one can

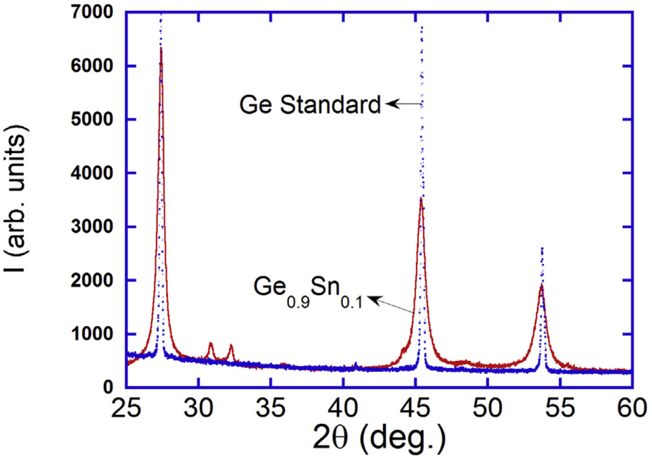

Fig. 1. Powder XRD of 90 at.% Ge+10 at.% Sn mixture showing the null effect of ball milling on the solid solution formation.

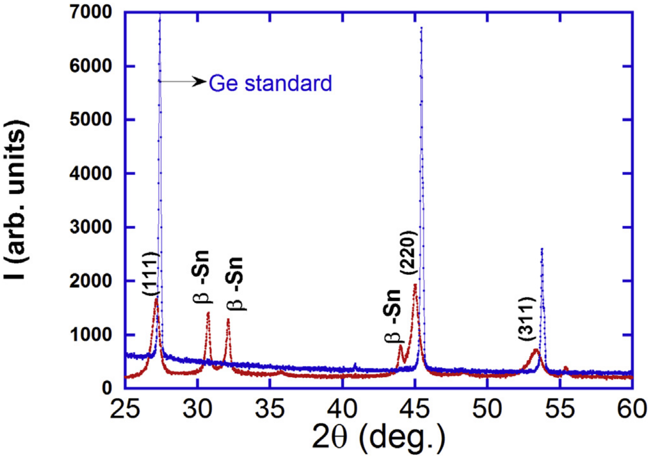

Fig. 3. Powder XRD of super saturated solid solution $Ge_{1-x}Sn_x$ with $x = 0.05$ along with the recorded XRD of Ge standard.

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