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FABRICATION OF LOW COST THERMOELECTRIC MATERIALS WITH IMPROVED PROPERTIES USING MODULATION-DOPING STRATEGY

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ABSTRACT

We introduce the modulation-doping strategy in bulk SiGe nanostructures to improve the thermoelectric power factor. By separating charge carriers from their parent atoms via embedding heavily doped nanoparticles inside an intrinsic host matrix, the ionized impurity scattering rate could be largely reduced, resulting in enhanced mobility. By band engineering, the carriers can spill over from nanoparticles into the host matrix, resulting in similar carrier concentrations, Fermi levels and consequently Seebeck coefficients as those of the uniform nanocomposites. In addition, nanoparticles with low thermal conductivities can further reduce the overall thermal conductivity of the sample. Combining the enhanced electrical conductivity, the reduced thermal conductivity and the unaffected Seebeck coefficient, we were able to enhance the thermoelectric properties of Si-rich $Si_{95}Ge_5$. And therefore were able to fabricate a low-cost sample with a competitive performance as those of the state of the art $Si_{80}Ge_{20}$.

NOMENCLATURE

Z	figure of merit
ZT	Dimensionless figure of merit
σ	Electrical conductivity
S	Seebeck coefficient
T	Absolute temperature
κ	Thermal conductivity
σS^2	Power factor

INTRODUCTION

The efficiency of thermoelectric materials is defined by their figure of merit ($ZT=\sigma S^2T/\kappa$). For a long time, ZTs of bulk materials were limited to values below one. In 1993, Hicks and Dresselhaus[1] proposed the use of low dimensional materials for thermoelectric applications which theoretically could have enhanced thermoelectric properties. Their work led to significant effort in fabrication and characterization of nanostructured materials. The original idea was to improve the power factor (σS^2). However, in practice, the higher figure of merit of the nanostructured materials was mainly a result of the reduced thermal conductivity. Introducing numerous interfaces of different sizes inside the material, can effectively scatter phonons of different mean free paths and reduce the thermal conductivity significantly[2]. The thermal conductivity of the thermoelectric materials has already been reduced to values below those of the alloy limit. At this point, we need strategies to improve the power factor of the thermoelectrics without deteriorating the low achieved thermal conductivity.

MODULATION DOPING

Modulation doping is widely used in microelectronics and photonic devices[3]. Traditional modulation structures are 2D structures where dopants are confined in a thin layer. The doped layer is separated by a spacer layer from the intrinsic channel layer. The heterointerface is located between the channel and the spacer and separates the two regions energetically[4]. Carriers then travel parallel to the film with much reduced impurity scattering and therefore with an enhanced mobility. We have recently applied a similar concept to bulk nanocomposite thermoelectric materials[5]. The main idea is to make a two-phase nanocomposite to spatially separate charge carriers from their parent atoms. These two-phase nanocomposites are made out of two different nanograins where dopants are incorporated only into one type. Using materials with proper band alignment, charge carriers flow from doped nanograins into the intrinsic region and travel through the intrinsic region with reduced impurity scattering. Most of the carriers would travel parallel to the interfaces and in the depleted regions of the intrinsic grains. However if the interfaces are close and the depleted regions are wide, they can cover the entire intrinsic region. In this case, carrier transport can happen through the entire intrinsic host grains. The reduced impurity scattering results in enhanced mobility and therefore enhanced electrical conductivity. If we keep the same overall number of carriers, we can maintain the Fermi level and therefore keep similar Seebeck coefficients as those of the uniform samples. Therefore the enhanced electrical conductivity results in the enhanced power factor.

The main challenge then is to maintain a low thermal conductivity. Nanostructured materials as discussed before have thermal conductivities much lower than their equivalent bulk samples. Introducing the modulation scheme can increase the thermal conductivity by increasing the electronic part of the thermal conductivity. The essence of modulation doping is to increase the charge carrier mobilities. Charge carriers are also heat carriers and therefore the increase in the carrier mobility will eventually increase the electronic part of the thermal conductivity. Besides metallic nanoparticles usually have very high lattice thermal conductivities. If we use high concentrations of metallic nanograins inside a low thermal conductivity material, it will result in enhanced lattice thermal conductivity which to the first order simply obeys the solid solution law.

In practice we need to limit our materials for both grain types to low thermal conductivity materials. Besides to accommodate the increase in the electronic part of the thermal conductivity, we need to reduce the lattice part of the thermal conductivity to values below those of the uniform nanostructured ones. For this reason, it is preferred that the two nanograins are made out of materials with the largest possible acoustic impedance mismatch to increase the interfacial resistance of dissimilar grains and reduce the lattice thermal conductivity below the values of the single phase nanocomposites.

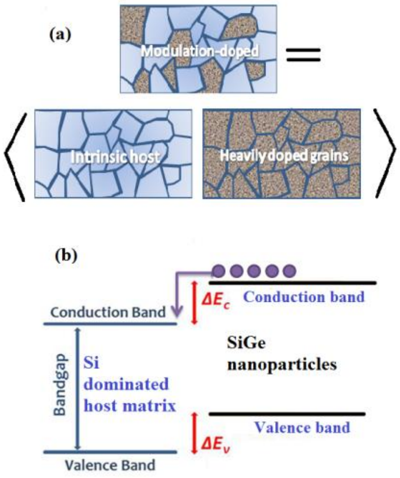

Figure 1. (a) Concept of modulating-doping in nanocomposites. One type of nanograins is heavily doped with a favorable potential such that free carriers enter the host, thereby improving the mobility of the carriers in the host due to reduced ionized impurity scattering. The thermoelectric properties of the modulation doping are obtained by averaging over the single-phase composites, as shown schematically. (b) Band alignment and charge flow schematically shown for n-type configuration.

EXPERIMENT

We applied the modulation doping idea to SiGe family of materials, both n and p-type. Boron (B) was used for p-type doping and phosphorous (P) for n-type doping. The nanostructured SiGe alloy and the B/P-doped SiGe nanoparticles are separately prepared by ball milling the appropriate raw materials for at least 10 h. Then the intrinsic SiGe alloy and the doped SiGe nanoparticles are mixed in the milling jar for a short time of about 10-30 min. The powder mixture is loaded into graphite dies with a 12.7mm central cylindrical opening diameter and is immediately pressed at temperatures of 1100-1250 C by a dc hot press method for rapid compaction of the nanopowders. The samples were characterized by high-resolution transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). The mass densities of these samples were measured using an Archimedes' kit. All samples have similar volume mass densities. The specimens used for TEM were prepared by dicing, polishing, and ion milling of the dc hot pressed bulk samples.

Samples are cut into 2 mm x 2 mm x 12 mm bars for four probe electrical conductivity and Seebeck coefficient measurements and into 12.7 mm diameter discs with appropriate thickness for thermal conductivity measurements. The electrical conductivity and Seebeck coefficient were measured by commercial equipment (Ulvac, ZEM-3) from room temperature to 900 ^{o}C; the thermal diffusivity was measured by a laser flash system (Netzsch LFA 457) from room temperature to 900 ^{o}C; the specific heat capacity was measured by a differential scanning calorimetry (DSC) method from room temperature to 600 ^{o}C.

RESULTS

Figure 1 shows a cartoon of the modulation-doping scheme which summarizes the idea of incorporating doped grains inside an intrinsic host matrix. The final composition can be treated as an average of the two types of grains. Figure 2 summarizes the results of applying the modulation scheme to n-type SiGe. As can be seen from the figure, modulation doping sample shows enhanced power factor compared to the equivalent uniform doped sample. The two samples have similar carrier concentrations and Seebeck coefficients. Therefore the enhancement is from the improved mobility. We were able to maintain the low thermal conductivity and as a result, 30% enhancement in the figure of merit compared to the equivalent sample was achieved. Moreover, the modulation doped sample has a 40% higher figure of merit compared to the optimally doped host matrix ($Si_{95}Ge_5$)[6] and can compete with the state of the art nanostructured $Si_{80}Ge_{20}$ sample[7] with much reduced Ge and therefore much lower fabrication cost.

In summary, we showed the effectiveness of 3D modulation doping to improve the power factor of thermoelectric materials. Combining the modulation scheme, with strategies to reduce the thermal conductivity, we were able to improve the figure of merit of n-type $Si_{95}Ge_5$ by 30%.

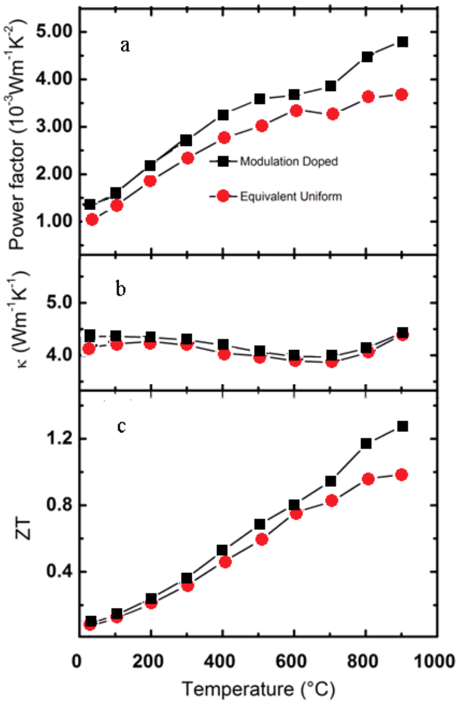

Figure 2. Temperature dependent (a) power factor ,(b) thermal conductivity κ and (c) ZT of modulation-doped $(Si_{95}Ge_5)_{75}(Si_{70}Ge_{30}P_3)_{35}$ nanocomposite sample, in comparison with those of equivalent uniform $Si_{86.25}Ge_{13.75}P_{1.05}$ uniform sample.

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