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Structure and thermoelectric properties of boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film

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The structure and thermoelectric properties of boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin films are investigated for potential application in microthermoelectric devices. Nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin films are grown by low-pressure chemical vapor deposition on a sandwich of $\text{Si}_3\text{N}_4/\text{SiO}_2/\text{Si}_3\text{N}_4$ films deposited on a Si (100) substrate. The $\text{Si}_{0.8}\text{Ge}_{0.2}$ film is doped with boron by ion implantation. The structure of the thin film is studied by means of atomic force microscopy, x-ray diffraction, and transmission electron microscopy. It is found that the film has column-shaped crystal grains ~ 100 nm in diameter oriented along the thickness of the film. The electrical conductivity and Seebeck coefficient are measured in the temperature range between 80–300 and 130–300 K, respectively. The thermal conductivity is measured at room temperature by a 3ω method. As compared with bulk silicon-germanium and microcrystalline film alloys of nearly the same Si/Ge ratio and doping concentrations, the $\text{Si}_{0.8}\text{Ge}_{0.2}$ nanocrystalline film exhibits a twofold reduction in the thermal conductivity, an enhancement in the Seebeck coefficient, and a reduction in the electrical conductivity. Enhanced heat carrier scattering due to the nanocrystalline structure of the films and a combined effect of boron segregation and carrier trapping at grain boundaries are believed to be responsible for the measured reductions in the thermal and electrical conductivities, respectively. © 2006 American Institute of Physics. [DOI: 10.1063/1.2337392]

I. INTRODUCTION

Silicon-germanium thin films have been proposed for energy conversion applications such as microthermoelectric devices^{1,2} or solar cells.³ Thermoelectric micropower generators are attractive because they have no moving parts, may operate at large power densities, and can use various heat sources.^{4,5} Compared to other thermoelectric materials, silicon-germanium alloys can sustain high operating temperatures and are compatible with metal-oxide-semiconductor (CMOS) processing. Moreover, quantum and classical size effects on electrons and phonons in such thin films, particularly superlattices, may further improve their thermoelectric performance.^{6,7}

The performance of thermoelectric generators depends on the thermoelectric figure of merit of the material, ZT , which is defined as $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal

conductivity, and T is the absolute temperature. The product $S^2\sigma$ is defined as the power factor. The power factor should be maximized, while the thermal conductivity should be reduced in order to achieve high efficiency thermoelectric devices. Previous studies performed on silicon-germanium microcrystalline alloy films showed that the power factor increases with doping, but for heavily doped films, the power factor reaches a limit which is not significantly dependent on the Ge mole fraction.^{8,9} This is because the electrical conductivity increases, while the Seebeck coefficient decreases with higher dopant concentrations and a lower silicon mole fraction. A significant reduction in thermal conductivity without a similar degradation of electrical transport properties could lead to further enhancements of the figure of merit. Further reduction of thermal conductivity can be realized by smaller grain size to limit phonon mean free path. This work investigates the effects of reducing the grain size of the film, below 100 nm, on thermoelectric properties.¹⁰

The structure and thermoelectric properties of boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin films are reported. Nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin films deposited by low-

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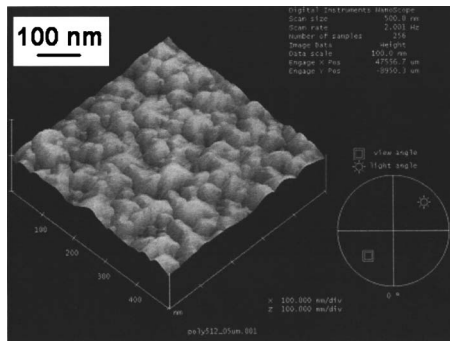


FIG. 1. Surface topography of the nanocrystalline silicon-germanium thin film performed on the as-grown film by atomic force microscopy (AFM).

pressure chemical-vapor deposition (LPCVD) are doped by ion implantation with high concentrations of boron. The structure of the thin film is studied by means of atomic force microscopy (AFM), x-ray diffraction (XRD), and transmission electron microscopy (TEM). Test structures are micro-fabricated for thermoelectric transport characterization of the $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film. The electrical conductivity and Seebeck coefficient are measured in the temperature range between 80–300 and 130–300 K, respectively. The in-plane electrical conductivity is determined by a four-point-probe method. The Seebeck coefficient is measured by applying a temperature gradient along the in-plane direction, while monitoring the resulting Seebeck voltage. The thermal conductivity is determined at room temperature by a 3ω method in the cross-plane direction. Details on the sample preparation and structural characterization are presented in Sec. II, while thermoelectric measurements are discussed in Sec. III.

II. SAMPLE AND STRUCTURAL CHARACTERIZATIONS

A. Film growth

The $\text{Si}_{0.8}\text{Ge}_{0.2}$ samples are grown by LPCVD on a $\langle 100 \rangle$ -oriented silicon wafer (6 in.). First, a sandwich structure of a $0.2 \mu\text{m}$ thick Si_3N_4 , a $0.4 \mu\text{m}$ SiO_2 , and $0.2 \mu\text{m}$ Si_3N_4 is deposited on the substrate for stress reduction and etch protection during the thermoelectric test structure microfabrication. Second, a 3 nm amorphous silicon film is deposited to prevent the formation of three-dimensional growth (island structures) during the nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film deposition.^{11,12} The amorphous film is grown at 575°C using a gas mixture of SiH_4 and H_2 with a flow rate of 50 SCCM (standard cubic centimeters per minute at STP) and 30 slm, respectively. Third, 200 nm of nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is grown at 550°C by adding 30% diluted GeH_4 in H_2 at 10 SCCM to the gas mixture used to grow the amorphous silicon film.

B. Structural characterization

The silicon and germanium mole fractions are verified by Rutherford backscattering (RBS) as 80% silicon and 20% germanium. Surface topography measurements of the nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film are performed on the as-grown film by AFM. The sample exhibits small grain structures

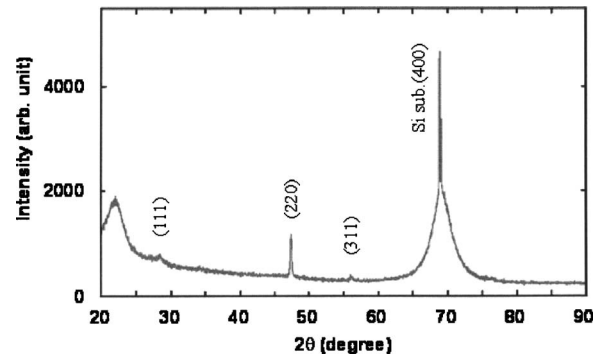


FIG. 2. X-ray diffraction pattern of boron doped nanocrystalline silicon-germanium thin film.

ranging in size from 20 to 100 nm, with a roughened surface, but no indications of three-dimensional (3D) growth are present (see Fig. 1).

Ion implantation is performed with boron at 1.5×10^{15} ions/cm² and 40 KeV, after patterning the film by plasma etching for the microfabrication of the thermoelectric test structures. Then, the sample is annealed at 900°C for 1 h in nitrogen ambient. The boron concentrations in the thin film are verified by secondary ion mass spectroscopy (SIMS). In this analysis, a thin polycrystalline silicon film deposited in similar conditions and with the same thickness as the nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is used as a dummy sample. The measured average concentration of boron is determined to be $4.3 \times 10^{19} \text{ cm}^{-3}$.

Investigations of the structure of the boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin films are performed by means of XRD and TEM. The crystallization and orientation of the thin film are studied by XRD (Fig. 2). The XRD step scans of the thin film are found to exhibit mainly a singular peak, corresponding to the $\{220\}$ plane. The other peaks, corresponding to $\{111\}$ and $\{311\}$ planes, are only slightly exhibited, indicating that the crystals in the film have a $\{220\}$ preferred orientation. The cross sectional structure of boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is investigated by TEM (Fig. 3). The figure shows that the thin film has a columnar grain structure with some randomly arranged small grains between the columnar grains. The size of the crystal grains reach up to 100 nm, consistent with the AFM surface characterization result.

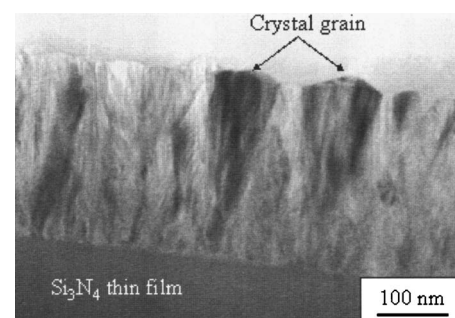


FIG. 3. The cross-sectional structure of boron doped nanocrystalline silicon-germanium thin film by transmission electron microscopy.

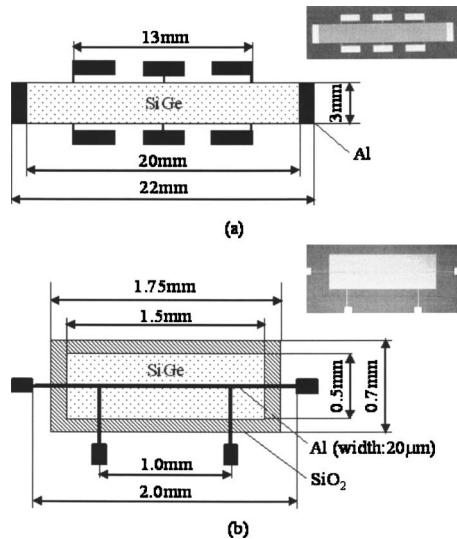


FIG. 4. The schematic of the microfabricated thermoelectric test structure. (a) Electrical conductivity and Seebeck coefficient, and (b) Thermal conductivity.

C. Test structure fabrication

A microfabricated test structure is employed to determine the in-plane electrical conductivity, in-plane Seebeck coefficient, and the cross-plane thermal conductivity of the boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film. To fabricate the test structure, the thin film is patterned by plasma etching using a photoresist mask. Next an aluminum film is deposited by sputtering and patterned by plasma etching. In order to reduce the electrical contact resistance between the aluminum film and the $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film, the natural oxide layer on the $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is removed just before the aluminum deposition by dipping the sample for 15 s in a hydrochloride solution. Different structures are patterned in the aluminum film to serve either as electrodes for electrical characterization, heater and temperature sensors for thermal conductivity characterization, or voltage probes for Seebeck characterization. Figure 4 shows a schematic of the microfabricated thermoelectric test structure.

III. RESULTS AND DISCUSSION

The in-plane electrical conductivity of the thin film is measured by a four-point-probe method at temperatures between 80 and 300 K. The sample size is 22 mm long, 3 mm wide, and $0.2 \mu\text{m}$ thick. A current passes between two outer electrodes, while the voltage drop is measured by two inner electrodes 13 mm apart, patterned between the two outer electrodes. Figure 5 shows the electrical conductivity dependence of temperature in the in-plane direction of the boron doped $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film. In heavily doped semiconductor films, electrical conductivity typically decreases with increasing temperature because the mobility decreases, while the concentration of charge carriers is almost constant. However, the electrical conductivity of the film investigated in this article increases slightly with temperature. One possible explanation may be a reduction in the effective concentration of the extrinsic charge carriers due to segregation of the dopant at the grain boundaries. For instance, a boron activation

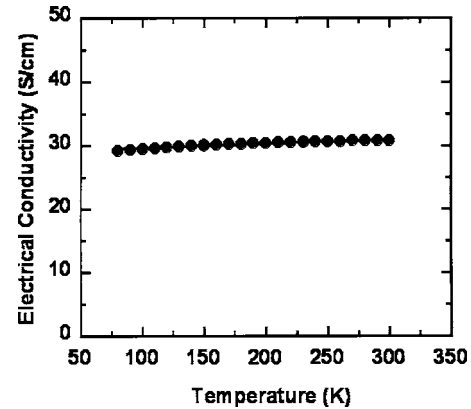


FIG. 5. The electrical conductivity dependence of temperature in the in-plane electrical conductivity of the boron doped silicon-germanium thin film ranging between 80 and 300 K.

of 47% for doping concentrations of $5 \times 10^{20} \text{ cm}^{-3}$ was reported for $\text{Si}_{0.5}\text{Ge}_{0.5}$ films with an average grain size of $1 \mu\text{m}$.⁸ The effect of boron dopant segregation to grain boundaries may be enhanced in the case of nanocrystalline films because a larger grain surface area per unit volume is available. However, measurements of the effective hole concentrations must be performed to validate this assumption. At 300 K, the electrical conductivity of the thin film is 30.9 S/cm. This value is relatively low by 10% compared to the electrical conductivity of bulk silicon-germanium alloy of similar boron doping concentration.⁹ A direct comparison with electrical conductivity of other doped silicon-germanium films is difficult because films with both a similar mole fraction and doping level were not reported. The measured electrical conductivity at room temperature is approximately seven times lower than reported for a $\text{Si}_{0.5}\text{Ge}_{0.5}$ microcrystalline film doped with boron at $5 \times 10^{19} \text{ cm}^{-3}$. Since the electrical conductivity for a given doping concentration was shown to decrease with an increase in the silicon mole fraction in microcrystalline silicon germanium films,⁸ perhaps this effect together with the reduced electrical activation of boron may explain in part the measured electrical conductivity reduction. On the other hand, trapping of charge carriers at the grain boundaries is a major cause for scattering of charge carriers in polycrystalline films. The smaller grains exhibited by the nanocrystalline film would lead to more scattering centers per unit volume and a reduction in electrical conductivity.

The Seebeck coefficient is measured by applying a temperature gradient along the sample in the in-plane direction and evaluating the resulting voltage. The inset of Fig. 6 shows the sample configuration for Seebeck coefficient characterization. A heater is attached to one edge of the sample, and the other edge of the sample is fixed on a copper heat sink. The voltage drop is measured between two electrodes that are separated by 13 mm, located near the center of the sample. Two thermocouples are also attached to the $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film with the same separation as the two voltage measurement electrodes. The temperature difference between the thermocouples is varied from 1 to 5 K, while the Seebeck voltage is recorded at each temperature difference. The Seebeck coefficient is estimated from the V - K slope.

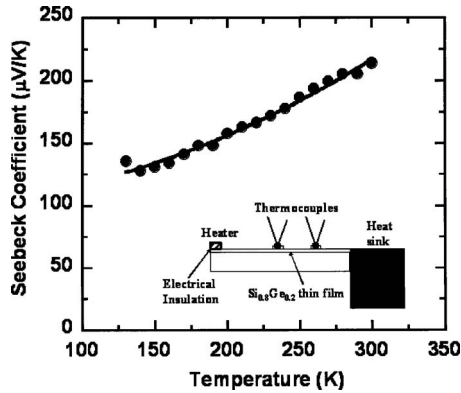


FIG. 6. Seebeck coefficient dependence of temperature in the in-plane direction of the boron doped silicon-germanium thin film ranging between 130 and 300 K.

Figure 6 presents the Seebeck coefficient dependence of temperature in the in-plane direction of the boron doped $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film ranging between 130 and 300 K. The absolute value of the Seebeck coefficient of the thin film increases with rising temperature. At 300 K, the Seebeck coefficient of the thin film is $221 \mu\text{V}/\text{K}$. Seebeck coefficient of the thin film is equivalent to the value of bulk silicon-germanium alloy⁹ and is ~ 2.4 times higher than a $\text{Si}_{0.75}\text{Ge}_{0.25}$ microcrystalline film doped with boron at $1.6 \times 10^{20} \text{ cm}^{-3}$ confirming the inverse dependence of Seebeck coefficient on carrier concentration.⁸

The cross-plane thermal conductivity of the boron doped $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is measured by a differential 3ω method.^{13,14} Aluminum heaters of $20 \mu\text{m}$ in width and 2 mm in length are deposited on the sample. A $0.2 \mu\text{m}$ SiO_2 is used to electrically insulate the sample from the heater. A reference sample of identical structure without the boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is used as the reference to subtract the unknown thermal properties of the insulation layers. Figure 7 shows (with data points) experimentally measured temperature amplitudes experienced by $20 \mu\text{m}$ wide heaters deposited onto the reference and the boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film sample. The thermal conductivity of the thin film is extracted from the best fit between the measured temperature difference and predictions of a heat conduction model, using the unknown thermal con-

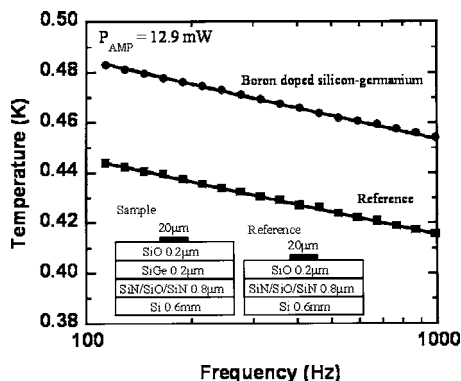


FIG. 7. The temperature amplitudes experienced by $20 \mu\text{m}$ wide heaters deposited onto the reference and the boron doped nanocrystalline silicon-germanium thin film sample.

ductivity of the thin film as a fitting parameter. In this work, both one-dimensional and two-dimensional heat conduction models have been used to extract the thermal conductivity of the thin film.^{14,15} However, it is found that the thermal conductivity values determined using the one-dimensional heat conduction model are $\sim 10\%$ larger compared with the determinations based on the two-dimensional model, although the heater width is 100 times larger than the thickness of the boron doped $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film. This is because the boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is sandwiched between layers with low thermal conductivity, a configuration which enhances the in-plane spreading of heat. This effect is not taken into account by the simple one-dimensional model. The lines in Fig. 7 are predictions of the temperature response of the heater using the two-dimensional heat conduction model and the fitted values for the thermal conductivity of the thin film. Isotropic thermal property of the boron doped $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film has been assumed. However, anisotropic film properties may be induced by the anisotropic grain structure. For instance, in thick chemical-vapor deposited (CVD) diamond films with columnar grain structures, the in-plane thermal conductivity was 50% smaller than the cross-plane thermal conductivity.¹⁶ On the other hand, isotropic properties have been reported in other films.^{17,18} A two-wire differential 3ω method^{14,19,20} may be used in the future to determine both in-plane (along the film plane) and cross-plane thermal conductivities of the boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film. The two-dimensional fitting also employs experimentally measured values for the thermal conductivity of the substrate and the dielectric films (SiO_2 , and the $\text{Si}_3\text{N}_4/\text{SiO}_2/\text{Si}_3\text{N}_4$ film sandwich), which are determined by fitting the frequency dependent temperature rise of the heater deposited on the reference sample. To simplify the fitting procedure, it is assumed that the dielectric films all have the same thermal conductivity and an average value of $1.9 \text{ W}/\text{m K}$ has been inferred for the dielectric films. This strategy capitalizes on the advantage of the differential technique that the measured thermal conductivity of the thin film of interest is relatively less affected by uncertainties associated with the thermal properties of the substrate and other films.¹⁴ The thermal conductivity experiments presented in this work are carried out at room temperatures. A value of $4.0 \times 10^{-3} \text{ K}^{-1}$ for the temperature coefficient of resistance of the aluminum heaters have been used to calculate the experimental heater temperature rise. The determined thermal conductivity of boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is $2.9 \text{ W}/\text{m K}$. The uncertainty of the thermal conductivity measurement using the 3ω method is estimated to be $\sim 20\%$.¹⁴ Compared to bulk alloys, the thermal conductivity of the thin film is about a factor of 2 smaller.⁹ The thermal conductivity is also four times smaller than the thermal conductivity along the planes of an undoped $\text{Si}(8 \text{ nm})/\text{Ge}(2 \text{ nm})$ superlattice,⁶ while it is 15% larger than the thermal conductivity across the planes of the same superlattice. Enhanced phonon scattering at the grain boundaries in the nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is believed to be responsible for the observed reduction in thermal conductivity as compared with bulk alloy and the in-plane thermal conductivity of a superlattice with a similar silicon mole fraction.

An estimate of the figure of merit can be made using the values measured for the electrical conductivity, Seebeck coefficient, and thermal conductivity, with the caution that the thermal conductivity was not measured along the same direction as the electrical transport properties. Assuming that the in-plane thermal conductivity is the same as that of the cross plane, the figure of merit of the thin film at 300 K is calculated to be $ZT=0.02$. This value is smaller than for bulk SiGe alloys at room temperature ($ZT=0.05-0.1$). The major factor in the reduction of ZT is the low electrical conductivity of the nanocrystalline thin film.

IV. CONCLUSION

The structure and thermoelectric properties of the boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film are studied for their potential applications in micropower generators. The structure of the boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is studied by means of atomic force microscopy, x-ray diffraction, and transmission electron microscopy. This thin film has mainly columnar grain structure and its grain size reaches up to 100 nm. Then we measure the thermoelectric properties of the boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film. The room temperature electrical conductivity of the thin film is low by 10% and its Seebeck coefficient is equivalent to that of bulk silicon-germanium material of similar doping concentration. The cross-plane thermal conductivity of the boron doped nanocrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is measured using the 3ω method. The room temperature thermal conductivity of the thin film is 2.9 W/m K. Compared to bulk alloys, the thermal conductivity of the thin film is about a factor of 2 smaller. The in-plane thermal conductivity may be further reduced due to the columnar structure of the grains. Enhanced heat carrier scattering due to the nanocrystalline structure of the films and a combined effect of boron segregation and carrier trapping at grain boundaries are believed to be responsible for the measured reductions in the thermal and electrical conductivities, respectively.

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