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論文内容の要旨

Thermoelectric materials have an excellent ability to convert thermal energy to electrical energy and vice versa. Noting that more than 60% of the energy produced in the world is disposed of without being used as waste heat, in recent years, expectations for thermoelectric conversion used as a waste heat recovery technology or an energy acquisition technology from unused heat have been glowing. Silicon (Si) is non-toxic and can behave as P-type or N-type semiconductor by adding a small amount of impurity element. Si has tended to be left out of candidates of materials for thermoelectric conversion modules due to its high thermal conductivity so far. However, because of its abundance and nontoxicity, it is attracting much attention for thermoelectric use for the future society. Recent studies have shown that effective heat transfer coefficient can be improved by making Si porous to compensate

for the disadvantage of high thermal conductivity, and hence use of Si as thermoelectric material could be realized in the not too distant future. Therefore, it is necessary to prepare data for the use of porous Si in thermoelectric devices. There are three major challenges in the fabrication of porous Si devices: fabrication of porous Si, the bonding of Si to metal electrodes, and device design. In this paper, we conducted investigations for the fabrication of devices using porous Si.

First, fabrication of porous Si and Si-B by unidirectional solidification under hydrogen atmosphere was conducted. In this technique, discontinuous decrease in the solubility of hydrogen at the freezing point is utilized for the formation of hydrogen pores elongated unidirectionally in the direction of solidification. The porosity and the average diameter of the prepared sample were evaluated by image-J analysis following observation with optical microscope. And for Si, the influence of doping elements for tuning carrier concentration on the pore formation and the influence of hydrogen dissolved in the Si crystal on the electric properties were examined. As a result, it was found that porous Si-B with unidirectional pores can be produced by unidirectional solidification under a hydrogen atmosphere. The average diameter of pores becomes larger and the porosity increases with the distance from the cooling surface. There is no significant difference between Si and Si-B in porosity and average diameter. It is also found that the effect of B-doping on pore formation is not significant. Regarding electrical properties, first of all, it was found that the carrier concentration of porous Si doped with B, which contains hydrogen atoms as solutes, is significantly higher than non-doped Si. That is, B, which is often used as a dopant for Si for tuning carrier concentration, works as a dopant in porous Si as well. On the other hand, the measured carrier concentration in the B-doped sample tends to scatter. This is due to the segregation of B. Furthermore, it was confirmed that the residual hydrogen in porous Si and Si-B can be decreased by annealing process with vacuum evacuation. Regarding the relationship between electrical conductivity and porosity, the electrical conductivity decreases in the direction perpendicular to the porosity as the porosity increases.

Second, the bonding conditions of porous thermoelectric material and metal electrodes are examined. In order to fabricate thermoelectric conversion devices, the bonding of thermoelectric material and metal electrode is essential. In particular, silver (Ag) is one of candidates for metal electrodes because of its high electrical conductivity and the absence of intermediate compounds with Si. The bonding properties between Si and Ag at the atomic scale and the shear strength have been reported in the past. However, more data such as bonding strength and contact resistance are needed for fabrication of thermoelectric devices using porous Si and their use. The present study

investigates the diffusion bonding between Si and Ag. The bonding strength and interfacial electrical resistivity have been evaluated. Bonding between Si and Ag were executed using a diffusion bonding technique. Diffusion bonding was performed under a uniaxial pressure at a high temperature in an Ar atmosphere with various pressures for various periods. The bonding strength was measured with a tensile tester. The electrical resistances of bonded samples were measured using a thermoelectric measurement and evaluation system. As a result, the diffusion bonding was successfully made at 1103 K under unidirectional compression load. No intermediate phase was observed consistently with the reported Ag-Si equilibrium phase diagram. The bonding strength increases with increasing bonding time up to 90 min while it does not vary around 8 MPa with bonding time longer than 90 min for the bonding with a 20 MPa bonding pressure followed by slow cooling. Furthermore, the diffusion bonding between Ag and Si was found to satisfy the bonding strength required for thermoelectric devices using porous Si. The interfacial electrical resistivity is in the order of 10^{-10} Ωm^2 and there is no significant variation with bonding time. Thus, Ag is useful as metallic electrodes for Si.

Finally, porous Si devices were fabricated. In this porous thermoelectric conversion device, the thermal fluid flows through pores of the thermoelectric materials and exchanges heat. Increase in thermal interface is the greatest advantage. Alternately arranging porous Si-B (P-type) and Si-Sb (N-type) connected with the electrodes in between and thermal insulation material, the flow paths are formed in a direction perpendicular to the plate. High-/low-temperature fluids alternately flows in the path and causes the thermal electromotive force. Hand-drilled Si wafers were used as the porous Si (diameter 1.2 mm, porosity 9.38 %). The devices were fabricated in a size of 17 mm × 17 mm, with one Si-B and one Si-Sb bonded to each other with Ag. Hot (about 353 K) and cold (about 293 K) temperature fluids flowed through the device, and electrical voltages of an order of mV were obtained.

論文審査の結果の要旨

学位申請者橋本康孝氏は、ホウ素を添加して熱電特性を高めたシリコンを水素雰囲気において一方向凝固し、一方向に伸びた孔を有するロータスシリコンを作製し、ホウ素が孔形成に及ぼす影響及び残存水素が電気的特性に及ぼす影響がともに小さいことを明らかにした。次に、多孔質シリコンを用いて熱源と熱電材料間の熱伝達を高めた熱流体透過型の新しい熱電変換デバイスを作製するため、重要な基礎技術である金属電極(銀)とシリコンの接合について調査し、拡散接合法を用いて、接合するにあたり1103Kにおいて20MPaの荷重下90minの時間接合処理を行えば、上記デバイスでの使用における水圧に十分に耐えられる引張接合強度が得られること、シリコン-銀間の界面抵抗はシリコンの電気抵抗の10分の1以下であることを明らかにし、適切に接合したAgは本デバイスの電極として使用に耐えると結論した。次に、多孔質シリコンを用いて実際に熱電変換デバイスを試作し、低温と高温の水を流して特性測定を行った結果、電圧が得られることを初めて観測し、温水-冷水間の温度差から予想される値とよい一致をみた。

本論文は、以下に示す茨城大学大学院理工学研究科における博士学位論文の評価基準を満たしていることを審査会において確認した。

（１）研究の目的及び当該研究分野における位置付けが明確に記述されている。
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提出された論文は、多孔質熱電材料を用いた新たな熱電変換デバイスの実用化に向け大きく寄与した。研究内容にはオリジナリティがあり、新たな熱電変換デバイス作製における課題の同定と解決といった工学的に有用な知見を得ていること、また当該分野において十分な学識を有していることを試問により確認できた。

以上を総合して、橋本康孝氏の学位論文審査及び最終試験を合格と判定した。