Porous Silicon Formed by Metal Assisted Chemical Etching for Thermoelectric Power Generator

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論文内容要約

Thermoelectric generators utilize Seebeck effect that directly convert thermal energy to useful electrical energy. With the development of internet of things (IoT), the demand of high performance micro thermoelectric generators (μTEG) becomes more impendency. μTEG can act as a power source to charge the battery of IoT devices or even replace the battery. Generally, μTEG development utilizes thin thermoelectric films integrated with microfabrication process. However, commercial thermoelectric materials, such as Bi_2Te_3, are lack of corresponding standard and equipment to integrate into microfabrication process. Moreover, their rarity and high price also limits their large-scale production.

Silicon, as the foundation of semiconductor industry, is widely used in microfabrication process. In addition to its cheap price, it is always considered as one of alternative thermoelectric materials. However, silicon isn't regarded as a thermoelectric material due to its high thermal conductivity. Until recently, nanostructured silicon that shrinks material dimensions to nanometer can incredibly enhance its thermoelectric performance by decreasing the thermal conductivity while sustaining its electrical conductivity. Porous silicon is one type of nanostructured silicon that is high potential for thermoelectric application arises from its low thermal conductivity. According to previous work, some reported porous silicon that has order nanopores arrays by dry etching can own good thermoelectric properties. Nevertheless, that precise dry etching technique is not fitted for most research group. In general, most reported porous silicon is synthesized by traditional electrochemical method, which cannot be regarded as a thermoelectric material due to the ultralow electrical conductivity. Moreover, non-ohmic contact between porous silicon and metal also impedes the development of thermoelectric applications. Metal assisted chemical etching (MACE) is novel wet etching process and silicon nanowires fabricated by MACE have been proved that own high figure of merit ZT. Therefore, in this thesis, MACE is used to fabricate porous silicon for increasing its thermoelectric performance and the contact problem occurred in porous silicon is solved.

Another obstacle is that the integration of nanostructured silicon into thermoelectric devices is a hard task. For example, to fabricate silicon nanowire's micro TEG (μTEG), its fabrication method is not just considered in the diameter of nanowires, but in the three dimensions. Namely, width and length of silicon nanowire are constrained to the micrometer regime, which makes difficult for the formation of a wide electronic path to circulate current and a long thermal path to sustain thermal gradients in silicon nanowire's μTEG. Therefore, most reported diverse silicon nanowire's μTEGs are fabricated by complicated fabrication process and expensive equipment. That strict fabrication condition is one reason that the numbers of successful silicon based μTEG is rare. In thesis, μTEG with a simper fabrication process that can have relatively high-power density is designed.

By solving the afore-mentioned challenges, this research aims at developing micro thermoelectric power generator based on porous silicon from many approaches as follow:

To optimize the structure of porous silicon for better thermoelectric performance, porous silicon is synthesized by metal assisted chemical etching ((MACE). MACE is a wet method that uses a noble metal as the catalyst for etching of semiconductor material. Compared with electrochemical method, porous silicon synthesized by MACE has more straight and uniform pores without branching. Three devices are fabricated to measure the thermoelectric properties of porous silicon. Porous silicon with different porosities and thicknesses are obtained by adjusting Ag deposition time and HF etching time. It shows that with increasing the porosities of porous silicon, the Seebeck coefficient can increase to 780 μV/K at the porosity of 38%, but the electrical and thermal conductivity continually decreases. The maximum ZT value of porous silicon can attain 0.02 when the porosity is 38%, which is 8 times greater than original silicon substrate. In addition, similar trend of thermoelectric properties is reflected with increasing of the thickness. Meanwhile, the reduction of electrical conductivity is larger than thermal conductivity. Therefore, the maximum ZT should be considered at low thickness of porous silicon.

Considering the low electrical conductivity of porous silicon, improving its electrical conductivity is expected to enhance thermoelectric performance. Moreover, non ohmic contact always occurs between porous silicon and metal. Therefore, electrical conductivity of porous silicon can be increased by decreasing contact resistance from non ohmic contact. In this chapter, spin on dopant (SOD) doping was used to modify the surface of porous silicon. An integrated measurement platform replacing previous three devices are used to measure thermoelectric properties. Compared with undoped porous silicon, p- and n-type doped porous silicon can achieve ohmic contact. Therefore, their electrical conductivity can increase to 1160 and 1390 S/m, respectively. Even though the Seebeck coefficient decreases, sustaining thermal conductivity results in the improvement of ZT value. For n-type, the ZT of porous silico via SOD doping can attain 0.025. For p-type, the ZT can attain 0.062 at room temperature which is the maximum value of porous silicon reported before.

Finally, porous silicon is firstly applied to fabricate micro thermoelectric power generators (μTEG). μTEG based on porous silicon has been successfully fabricated that is more efficient than that of other reported silicon based μTEGs. Moreover, it has high potential to fabricate large area μTEG based on simpler integrate method. For comparison, μTEG based bulk silicon is also fabricated. When the harvested temperature difference is in the range of 2~4℃, the maximum power density of porous silicon and bulk silicon based μTEGs is 1.12μw/cm^2 and 0.18μw/cm^2, respectively.

In summary, this thesis has successfully fabricated thermoelectric power generator based on porous silicon synthesized by

MACE. high ZT value and new devices of porous silicon are expected to open up opportunities for diverse thermoelectric applications combining with microfabrication industry.