主論文の要約

論文題目　**Investigation on Thermoelectric Properties Improvement of Group IV Alloy Thin Films**
(IV 族混晶薄膜の熱電特性改善に関する研究)

氏　　名　**彭　英**

論文内容の要約

The interest in thermoelectrics for an electrical output power by converting any kind of heat has flourished in recent years, but questions about the efficiency at the ambient temperature and safety remain unanswered. With the possibility of integration in the technology of semiconductors based on silicon, highly harvested power density, abundant on earth, nontoxicity, and cost-efficiency, in this study, Si-based films doped with Ge and Sn have been investigated to highlight their efficiency through magnetron sputtering, ion implantation, and high-temperature rapid thermal annealing (RTA) process.

The chapter 1 is the introduction chapter. Firstly, I describe the basic parameters of thermoelectric phenomenon and the interdependence of each other, such as Seebeck coefficient, electrical conductivity, thermal conductivity, ZT value, and so on. Then, I introduce the research status and development trend of thermoelectric materials by taking block thermoelectric materials − low dimensional thermoelectric materials − flexible thermoelectric materials as the main line. The last part of the first chapter is the purpose and breakthrough point of my research, and summarizes the original and significance of this research.

The chapter 2 is the introductions of material preparation, measurements, systems and techniques in this study. I first introduce the experimental framework of this study and show the preparation process of Si/Ge multilayer film and SiGeSn monolayer film. Next, I introduce the working principle of magnetron sputtering equipment and the detailed parameters of thin film preparation in this paper. The following is the introduction of the principle of ion implantation machine and the simulation analysis of ion implantation parameter selection in this paper. At the end of the film preparation equipment introduction is a brief description of the rapid thermal annealing equipment. In the third section of chapter 2, I introduce the relevant equipment and test parameters for the physical properties analysis of thin films, such as XRD, Raman, SEM, TEM, and so on. The fourth and fifth sections of the second chapter of this paper mainly introduce the instruments and equipment for testing the thermoelectric performance of the film samples for testing Seebeck and thermal conductivity, and TDTR technology for testing the thermal conductivity of the film.

In the chapter 3, the improvement of the thermoelectric properties of Si/Ge multilayer films was studied. I conducted an in-depth study on the thermoelectric performance improvement of Si/Ge multilayer films at near-room temperature, by following the process of film preparation, film characterization and film thermoelectric performance test and analysis. The conclusions of the chapter 3 is that B-doped Si/Ge multilayer films have been successfully prepared by magnetron sputtering and rapid thermal annealing. I determined the presence of nanostructures by XRD analysis, Raman spectroscopy, and TEM, and obtained a new structure by optimizing the preparation processes. It had a multilayer structure of five periods, each of which consisted of 10.2 nm-thick 40% B-doped Si ($Si_{60}B_{40}$), 1.1 nm-thick B, and 13 nm-thick 15% B-doped Ge($Ge_{85}B_{15}$) layers. The quantum dots embedded in the multilayered structure achieved by rapid thermal annealing exhibit an excellent thermoelectric performance at approximately near room temperature, which is comparable to that of bulk $Si_{1-x}Ge_x$ in the high-temperature range. This Si/Ge film caused interface scattering, interface barrier formation, and quantum dot confinement, which improved the thermoelectric properties with the maximum power factor up to 5.6×10^{-2} W/mK^2.

Although in the chapter 3, the thermoelectric performance of Si/Ge multilayer films at near room temperature has been significantly improved, there are still some problems, such as Ⅰ. the superlattice structure is complex; Ⅱ. the content of Ge in Si/Ge multilayer films is more than 60%, because the price of Ge is several hundreds times higher than Si, the cost of the films are very higher; Ⅲ. although the thermoelectric performances of the Si/Ge multilayer films are outstanding at 200 °C, however, further research is needed to improve the performance of silicon-based thermoelectric materials at room temperature. The introduction of Sn into $Si_{1-x}Ge_x$ not only significantly improves the conductivity of $Si_{1-x}Ge_x$ thermoelectric materials at room temperature but also provides a relatively high Seebeck coefficient possible by the increasing of grain size due to the liquid Sn in high temperature accelerating the growth of $Si_{1-x}Ge_x$ grain. Thus, in the chapter 4, I turned to the research of SiGeSn single layer films with low Ge content (10%) and the B ion implantation technology. In the chapter 4, after the process of film preparation, B ion implantation, film characterization and film thermoelectric performance test and analysis, I find that the polycrystalline $Si_{1-x-y}Ge_xSn_y$ films have been successfully deposited on Si/SiO_2 wafers. The synthesized $Si_{1-x-y}Ge_xSn_y$ films have a microcrystalline grain structures ranging in size from 7 to 24 nm. It shows that the introduction of Sn into $Si_{1-x}Ge_x$ can significantly improve the conductivity of $Si_{1-x}Ge_x$ based thermoelectric materials at room temperature while obtaining a relatively high Seebeck coefficient. A high power factor of 11.3 $\mu W\ cm^{-1}\ K^{-2}$ has been achieved for optimized samples at room temperature, the cost-effective and scalable techniques employed in this research point to future impact of the development of ambient thermoelectric materials both in academia and commercial.

Despite that in the chapter 4, I preliminarily found Sn introduced into $Si_{1-x}Ge_x$ can significantly improve the thermoelectric performance of $Si_{1-x}Ge_x$ films at room temperature, but there are still problems that how much Sn can better improve the thermoelectric properties of silicon-based films and the effect of boron ion implantation doses need further investigation. Therefore, in the chapter 5, I focus on research the thermoelectric performance evolution law of $Si_{1-x-y}Ge_xSn_y$ film in different Sn content, and the different ion implantation doses. In the chapter 5, I change the Sn content from 7.5% to 17%, adjust the ion implantation doses form 0.25×10^{15} to 8×10^{15} atoms/cm^2. After process of film preparation, B ion implantation, film characterization, and film thermoelectric performance test and analysis, I found that with the continuous increase of Sn content, modulation doping occurred. Thus, it demonstrates that the introduction of Sn into $Si_{1-x}Ge_x$ can significantly improve the conductivity of $Si_{1-x}Ge_x$ based thermoelectric materials at room temperature while obtaining a relatively high Seebeck coefficient due to the modulation-doping effect. At room temperature, a high power factor value of 19.5 $\mu W/cmK^2$ has been achieved, which is 1.7 times higher than the samples with the highest performances in the chapter 4. Therefore, the modulation doping effect caused by precipitation of Sn points the way for silicon-based thermoelectric materials to develop thermoelectric materials and devices at room temperature.

As confirmed in the chapter 3, quantum dots can significantly improve the Seebeck coefficient of silicon-based films at room temperature. In the chapter 5, it is discussed that the introduction of Sn into SiGe films can not only greatly improve the electrical conductivity of SiGeSn films at room temperature, but also reduce the thermal conductivity. Therefore, SiGeSn thermoelectric film with quantum dot nanostructure composite modulation doping mechanism is worthy of further systematic study. In addition, for SiGe alloy, generally ZT value of the n-type SiGe materials are significantly greater than p-type SiGe materials, thus in the chapter 6, I turn to the study of SiGeSn film with phosphorus ion implantation, expecting to innovatively improve the thermoelectric property of SiGeSn film at room temperature through the modulation doping mechanism composite quantum dots nanostructure. In the chapter 6, I designed that in the SiGeSn film ,the Ge content is 10%, the Sn content varying from 2.8% to 7.3%, and the phosphorus ion implantation dose from 2×10^{15} to 6×10^{15} atoms/cm^2.After the process of film preparation ,P ion implantation, RTA, I measured the thermoelectric properties of the sample and found that when the Sn content was 5.1% and the phosphorus ion injection dose was 4×10^{15} atoms/cm^2, the sample had extremely high thermoelectric properties. In order to reveal the reasons for the appearance of samples with high thermoelectric properties, I firstly used the XRD to analyze the samples, However, XRD results showed that after 2-15 seconds annealing at 1100 ℃, the grain size increased with the annealing time, but the grain size of each sample was not significantly different. Therefore, I further used TEM to analyze the nanostructure of the film. The TEM images show that the high-performance samples are rich in high-density and evenly distributed quantum dots of about 3 nm in size. The results of low temperature resistance and magnetic resistance tests also further confirm the existence of quantum dots and quantum effects. And then, at room temperature, a power factor of up to 847 μW/cmK^2 was obtained due to relatively high Seebeck coefficient and conductivity caused by the quantum confinement and modulation-doping effects. Thus, the subtle strategy, cost-effective and scalable technology, elaborate experiment used in this work points the way of promoting the academic and commercial applications of silicon-based thermoelectric materials.

The chapter 7 is the conclusion of the paper and the prospect of future research. In this paper, the conclusion of the 3-6 chapters show us that the thermoelectric properties of Si-based which deposited on hard Si/SiO$_2$ substrates have been greatly improved at room temperature, in the future, the research and development of flexible SiGeSn films deposited on flexible Si/SiO$_2$ substrates and thermoelectric devices will be put on the agenda to meet the huge market demand for providing electric energy for wearable devices.