Chapter III

Material Preparation and Characterization

3.1 Sample Preparation

3.1.1 Mechanical Alloying

A planetary ball mill was used for preparation of mechanical alloy for this work. Starting raw materials are iron powder (Goodfellow CAS No.7439-89-6, 98% + purity, -100 mesh size) silicon powder (Sigma Aldrich No.215619, 99+% purity, -325 mesh size), and cobalt powder (Sigma Aldrich No.266647, 99.9+% purity, -100 mesh size) as an n-type dopant designed to yield $Fe_xCo_{1-x}Si_2$ (x = 0, 0.01, 0.03, 0.05). Batches of 15.00 g of $Fe_xCo_{1-x}Si_2$ were milled for 50 hours under an Ar atmosphere to minimize oxidation. The ball size is 10 mm in diameter and the ball to powder weight ratio of 20:1 was used in all cases, rotation of milling vial at 295 rpm. During the milling, the mixtures stick to the inner wall of vial. After milling for every 5 hours, the mixtures were scratched off the wall by a stainless steal spoon and continue milling until the total milling times are 50 hours. Small amount of mixture was sampled at intervals and analyzed by the X-ray diffraction (XRD) and a Laser particle-size-distribution analyzer as to determine the state of mixture and predict the sufficient milling time.

3.1.2 Cold-pressing

After milling, the mixture was sieved to -80 meshes and batches of 1.62 g of each material were cold-compacted by a hydraulic-press in the room temperature air with the gauge pressure of 400 MPa into a rectangular bar of the size $15\times32\times1.5$ mm^3.

3.1.3 Thermal Heating

Samples were put on a silicon wafer which was inside a furnace. All samples were heat treatment at 900°C with heating rate of 10°C/min under the argon ambience at the pressure of 0.75-0.80 atm.

3.2 Sample Characterization

3.2.1 X-ray Diffraction (XRD)

In order to investigate the degree of alloying and phase transformation during milling and heating, X-ray diffraction (XRD) analysis was carried out for MA powders and heated samples. A Philips (X'pert) x-ray diffractometer system with Cu-Kα radiation (λ = 1.54060 A°) was used at 40 KV and 30 mA. We use PDF database as the reference for phase determination.

3.2.2 Laser Particle Size Analyzer

Particle size distributions of the mechanically alloyed powders were determined by Laser Particle Size Analyzer "Malvern" (Mastersizer S), The Malvern Mastersizer S uses the Small Angle Laser Light Scattering (SALLS) principle to measure particle size distributions of emulsions, suspensions, powders and aerosols. A 2 mW He-Ne red laser (633 nm in wavelength) with 18 mm beam diameter, collimated and spatially filtered to a single transverse mode is used as the incident light beam. The device uses either the Mie or Fraunhofer theory to interpret the scattering pattern. As such, particle sizes can be measured in the range of 0.05μm to 3.5 mm. In this research, the aggregated mixture was ultrasonically dissolved in water before the measurement.

3.2.3 Scanning Electron Microscope (SEM)

In order to investigate the grain size of heated material, a Jeol (JSM 5410LV) scanning electron microscope was used to observe the surface of detected $Fe_{0.95}Co_{0.05}Si_2$ which are heated for 10 minutes and 4 hours. We prepared sample by cutting it into specimens with dimensions suitable with stubs. Importantly tall samples can damage the objective lens pole piece if moved to high. Samples were stuck with stubs by electrically-conductive carbon tape. All samples were coated gold to make their surface conductive.

3.2.4 Thermopower Measurement

Thermopower (α) was determined by the ratio of an open-circuit potential difference to a temperature difference. The temperature difference is determined by using chromel-alumel (type K) thermocouples, and the copper branches are also used to obtain the potential difference which is shown in Figure 3.1. The reference junctions of the thermocouples fixed with a heat sink whose temperature is close to the room temperature. The potential differences between V_1 and V_2 can be read sequentially by a Keithley digital multimetor model 2700. The thermal gradient can be varied by heating the probe and take α as $dV_{12}/d(\Delta T)$. The principle relies on a heated probe-tip positioned on to the surface of a sample. The probe is connected to a thermocouple measuring the temperature T_1 at the probe tip. The bottom of sample makes a contact to a heat sink whose temperature T_0 is measured by another thermocouple. The Cu were used to measure the potential difference, ΔV, across the sample. A set up is for thermopower measurements over a temperature range 26-40°C.

We also used this design for measurements of thermopower up to 500°C but a set up was in the vacuum chamber. The temperature difference between T_1 and T_2 was less than 10°C. The electrical furnace was used to vary the base temperature of the system up to 500°C.

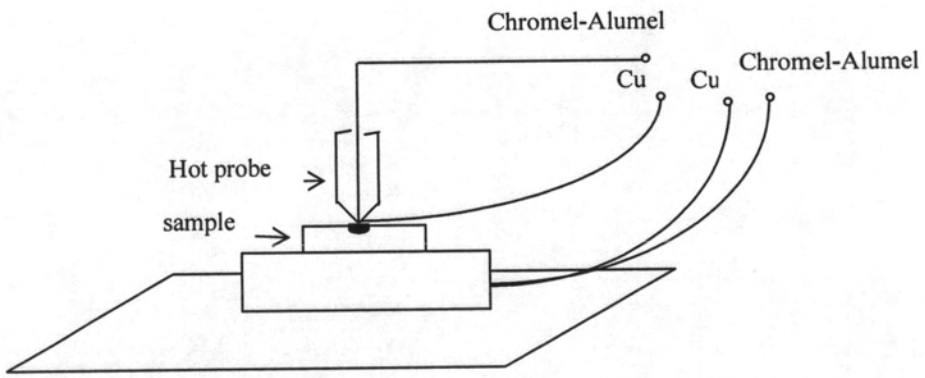

Figure 3.1: Hot probe to measure thermopower

3.2.5 Resistivity Measurement

To measure the resistivity of our samples, the four-probe measurement method is used. This method is described by attaching four leads to the sample shown in Figure 3.2. A current is fed between the outer two leads, while the voltage is measured between the inner two leads. Using Ohm's law one can calculate its resistance which is then multiplied by a correction factor to give the resistiviry.

$$\rho = G\frac{V}{I} \tag{3.1}$$

where G is a correction factor depending on sample shape and dimensions, and the arrangement of electrical contact [11].

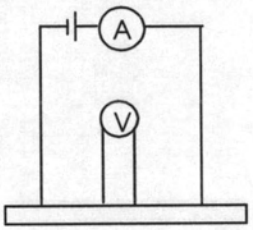

Figure 3.2: Schematic of standard four-probe resistance measurement approach

The dimension of sample is 4mm×8mm×1.5mm (wide×length×high). The spacing of probe ~ 1 mm. The separation of current and voltage contacts is fulfilled in the four-point method indicated in Figure 3.3

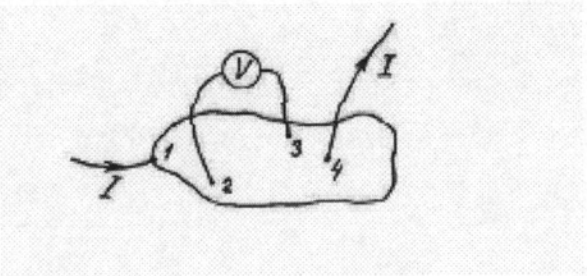

Figure 3.3: Four-point measurement

The resistivity is given by

$$\rho = \frac{V_{2-3}}{I_{1-4}} \tag{3.2}$$

where V_{2-3} is the voltage between contacts 2 and 3, I_{1-4} is the current through contacts 1 and 4.

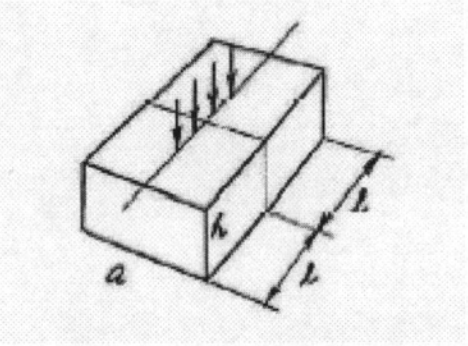

Figure 3.4: Figure of Four points in a bar of rectangular cross section

The geometric factor of rectangular cross section has been derived by Uhlir and Hansen [11]. Hensen's results are given in the form:

$$\rho = G\frac{V}{I} \tag{3.3}$$

$$G = \frac{2\pi s}{F} \tag{3.4}$$

$$F = (\frac{a}{s}, \frac{h}{s}, \frac{l}{s}) \tag{3.5}$$

The values of F for an infinitely long bar are shown at Figure 3.5. G is a correction factor dependent on sample shape and dimensions, and the arrangement of electrical contacts. S is spacing of probe.

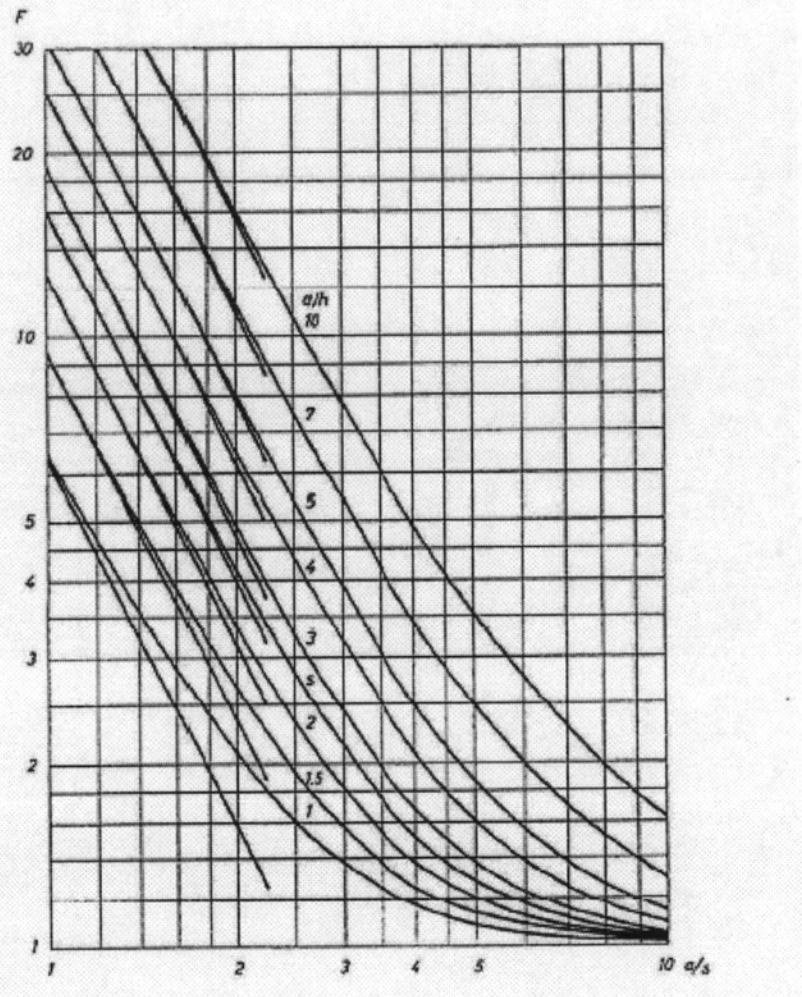

Figure 3.5: The correction factor for an infinite bar of rectangular cross-section a × h

3.2.6 Van der Pauw Resistivity and Hall Effect Measurement

Hall box is used measure van der Pawn resistivity and Hall voltage. We can switch the current source and the voltmeter to all sides of the sample by choose a knob of Hall box.

pole / configuration	1	2	3	4
(1)	I+	I-	V-	V+
(2)	V+	I+	I-	V-
(3)	V-	V+	I+	I-
(4)	I-	V-	V+	I+
(5)	I+	V+	I-	V-
(6)	V+	I+	V-	I-

Table 3.1: Configuration of Hall box

Data acquisition is via an IEEE 488.2 GPIB bus, which is one type of General Purpose Interface (GPIB). The GPIB carries two types of massages from the PC : device-dependent and interface massage. The PC defines and transmits these massages through LabVIEW6.1 programs, known as virtual instruments (VIs), that are created by a graphical programming language. The VIs consist of an interactive user interface (the 'front panel') which simulates the panel of a physical instrument, a data flow diagram (or the 'block diagram') that serves as the source code, and icon connections that allow VIs to pass data to subVI. The window of LabVIEW6.1 was shown in Figure 3.6.

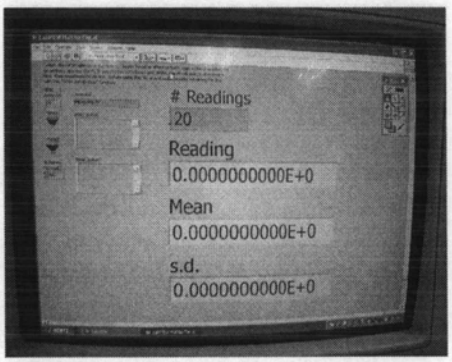

Figure 3.6: The window of program LabVIEW which is used in this experiment

3.2.7 Electrical Contacts

Silver paint (RS-186-3600) was used to provide electrical contact between the sample and Cu wire. A contact metal and a semiconductor have different work function. When the two materials are placed in contact, electron will flow from the one with the lower work function until the Fermi levels equilibrate. As a result, the material with the lower work function will take on a slight positive charge while that with the higher function will become slightly negative. The resulting electrostatic potential is termed the built-in field designated by V_{bi}. The built-in field is the cause of band-bending in the semiconductor near the junction. In this experiment I measure and record the I-V curve of 6 configurations in each sample. If a contact is ohmic a current varies linearly with voltage. Or if the I-V curve is non-linear and asymmetric, the contact can instead be termed Schottky contact.