The Effect of Annealing on Resistivity Measurements of $TiSi_2$ and TiN Using the collinear Four Point Probe Technique

Eman Mousa Alhajji

North Carolina State University

Department of Materials Science and Engineering

MSE 355 Lab Report

201

A

Dennis Szymanski

09/30/2016

Abstract

The objective of this experiment was to use the four-point probe technique to correlate how the annealing treatment and crystal structures affect resistivity and sheer resistance. Using S-301 SIGNATONE for the four-point probe contacts, KETHLEY 2000 MULTIMETER for voltage measurements and HP 6181C DC CURRENT SOURCE for a constant current supply, two $TiSi_2$ films, one annealed at 600 °C and one annealed at 800 °C, and two ceramic TiN films, one as deposited and one annealed, were examined. The average resistivity measured at the center of the $TiSi_2$ samples annealed at 600ºC and 800 ºC were determined to be 36.96 μΩ-cm and 15.58 μΩ-cm, respectively. Furthermore, the average resistivity measured at the center of the as deposited and annealed TiN samples were determined to be 16.805 μΩ-cm and 14.990 μΩ-cm, respectively. The annealing process is a method that can be a widely used to enhance the microstructure and improve the electrical properties by reducing the stresses and defects in the deposited films.

Introduction

Resistivity is a material property that measures how strongly a given material opposes the flow of electric current. [1] This material property, which is the inverse of conductivity, depends significantly upon the class of materials. In metals, the Fermi level lies in the conduction band giving rise to free conduction electrons. However, the Fermi level is within the band gap in semiconductors. For undoped semiconductors, Fermi level approximately halfway between the conduction band minimum and valence band maximum. For extrinsic semiconductors, dopant atoms increase the majority charge carrier concentration by donating electrons to the conduction band or producing holes in the valence band. [1,2]

One of the most useful techniques to measure resistivity in semiconductors is a four-point probe. [1] A four-point probe contains four thin collinearly placed tungsten wires probes, which are made to contact the sample under test as shown in Figure 1.

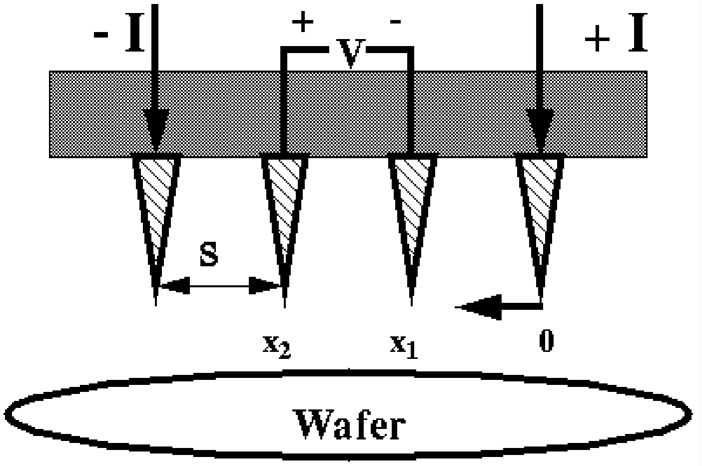

Figure 1. Schematic of a four-point probe. [1]

Current I is made to flow between the outer probes, and voltage V is measured between the two inner probes, with a high impedance multimeter, probe, spreading and contact resistances are negligible. If the sample is of semi-infinite volume where its thickness is less than half the probe spacing, the current emanates from the probes as rings with an area.[1] Combination of the integration of the differential resistance and Ohm's law gives the resistivity of the semi-infinite volume of thin conducting layers as the following:

$$\rho = 4.532t(V/I) \tag{1}$$

where t is the sample thickness, V is the voltage and I is the current. For a block of material that is uniformly doped and has resistivity ρ, the sheet resistance can be defined as $R_s = \rho/t$ with units of Ω/square and is given by

$$Rs = 4.532(V/I) \tag{2}$$

where V is the voltage and I is the current.

Titanium silicide ($TiSi_2$) is a material deposited and formed as a conductive layer during silicon microelectronics device fabrication. $TiSi_2$ exists in two different crystallographic forms, C49 and C54. Both are orthorhombic with a difference in lattice constant and atomic position.[1] Titanium nitride (TiN) is an extremely hard ceramic material, often used as a coating on titanium alloys, steel, carbide, and aluminum components to improve the substrate's surface properties. TiN films are deposited on a silicon substrate as well.[1,3]

The objective of this experiment was to use the four-point probe technique to measure the resistivity and sheet resistance to analyze how annealing treatment and crystal structures affect these properties. The samples examined were two titanium silicide films deposited on p-type silicon, one annealed at 600 °C and one annealed at 800 °C, and two ceramic TiN films, one as deposited and one annealed.

Experimental procedure

In this experiment, S-301 SIGNATONE was used for the collinear four-point probe contacts, KETHLEY 2000 MULTIMETER was used to measure voltage and HP 6181C DC CURRENT SOURCE was used as a constant current supplier. The samples used in the measurement of resistivity were titanium silicide film deposited on p-type silicon and annealed at 600 °C for 90 seconds, titanium silicide film deposited on p-type silicon and annealed at 800 °C for 30 seconds, ceramic TiN as deposited and Ceramic TiN annealed. Thickness of the $TiSi_2$ samples was 150 nm. Thickness of the TiN samples was 200 nm. The distance of separation between the probes was 1.7 mm. The experiment was performed at room temperature and a pressure of 1 atm.

First, the following steps were performed for each of the $TiSi_2$ samples. The sample was mounted on the stage of S-301 SIGNATONE. Using HP 6181C DC CURRENT SOURCE and KETHLEY 2000 MULTIMETER, four measurements for the voltage, starting with 1 mA of current and increasing current to 2 mA, 4 mA, and 6 mA near the center of the samples were taken and recorded. The voltage limit was set to 3 V. It was taken into consideration that the voltage across the input leads did not exceed the compliance voltage. It is worthwhile to note that if the compliance voltage is exceeded, the voltage limit light is on, indicating that the contacts are non-ohmic. [1] Contacts were made possible by stacking papers under the sample. The voltage in both forward and reverse current were measured and average of the two the voltages was used to cancel any thermal emf. Next, measurements for the voltage near the edge of the sample in a direction parallel to the probe spacing were repeated at 1 mA and 6 mA. Finally, for TiN samples, the measurements above were repeated on the center of the wafers at 10 mA and 60 mA.

Results and Discussion

Curves of voltage vs current of the four samples are shown in Figure 2. The linearity over the current range indicates ohmic behavior verifying Ohm's law. Voltage measurements were found to increase linearly with the increase of current. [1,2]

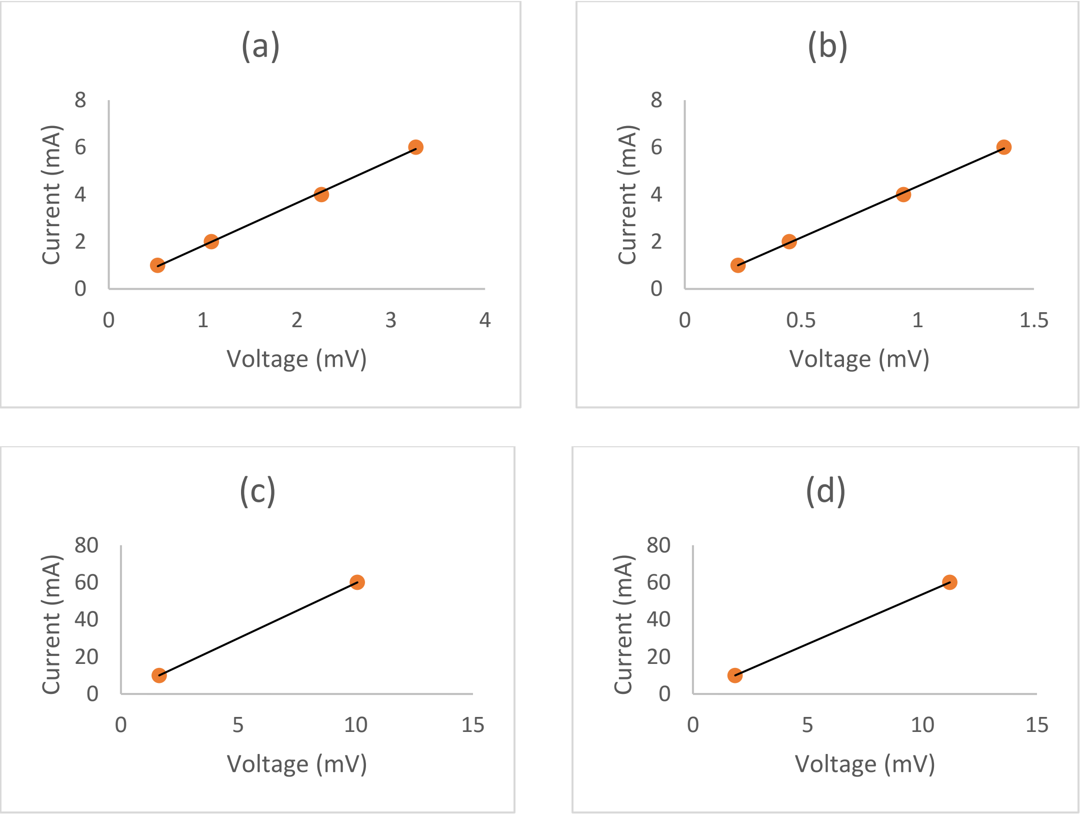

Figure 1. Linear curves of voltage (mV) vs current (mA) for (a) TiSi$_2$ annealed at 600 °C, (b) TiSi$_2$ annealed at 800 °C, (c) TiN annealed and (d) TiN as disposed.

The resistivity and sheet resistance for each sample were calculated using Equation 1 and Equation 2. As shown in both Table 1 and Table 2, the average resistivity measured at the center of the TiSi$_2$ samples annealed at 600ºC and 800 ºC were determined to be 36.96 μΩ-cm and 15.58 μΩ-cm, respectively. Correspondingly, the average sheet resistance measured at the center of the $TiSi_2$ samples annealed at 600ºC and 800 ºC were determined to be 2.463 Ω/sq and 1.039 Ω/sq, respectively. It was observed that the higher annealing temperature yielded lower resistivity and sheet resistance. Moreover, the values of sheet resistance and resistivity were approximately doubled when the voltages were measured at the edge of the $TiSi_2$ samples.

Table 1 : Resistivity Measurements for titanium silicide with a thickness of 1.5×10^{-5} cm annealed at 600ºC.

I (mA)	Forward Voltage (mV)	Reverse Voltage (mV)	Average Voltage (mV)	Sheet Resistance (Ω/sq)	Resistivity (Ω-cm)
1 at the center	0.518	0.523	0.520	2.358	3.538×10^{-5}
2 at the center	1.091	1.089	1.090	2.469	3.704×10^{-5}
4 at the center	2.261	2.261	2.261	2.561	3.842×10^{-5}
6 at the center	3.264	3.262	3.263	2.464	3.697×10^{-5}
1 at the edge	1.237	1.235	1.236	5.601	8.402×10^{-5}
6 at the edge	7.518	7.502	7.510	5.672	8.508×10^{-5}

Table 2 : Resistivity Measurements for titanium silicide with a thickness of 1.5×10^{-5} cm annealed at 800ºC.

I (mA)	Forward Voltage (mV)	Reverse Voltage (mV)	Average Voltage (mV)	Sheet Resistance (Ω/sq)	Resistivity (Ω-cm)
1 at the center	0.230	0.227	0.229	1.036	1.553×10^{-5}
2 at the center	0.451	0.448	0.449	1.019	1.527×10^{-5}
4 at the center	0.941	0.939	0.940	1.065	1.598×10^{-5}
6 at the center	1.373	1.370	1.371	1.036	1.554×10^{-5}
1 at the edge	0.261	0.260	0.261	1.181	1.771×10^{-5}
6 at the edge	1.550	1.552	1.551	1.172	1.757×10^{-5}

The different electrical conductivity of the resulting layers is a result of the difference in crystal structure. The maximum temperature during thermal processing of the $TiSi_2$ layer identifies the crystal structure. At the maximum temperature, the structure relaxes and the density of impurities and defect decreases, which corresponds to the decrease in resistivity and sheet resistance. The measurements were found to be consistent with the 600ºC and 800ºC annealing conditions forming the C49 of higher resistivity and C54 of lower resistivity structures, respectively. Different annealing temperatures produce difference in lattice constants, micro-strain in the film and the grain size. [1] These changes in structural parameters are responsible for the decrease of electrical resistivity in the annealed $TiSi_2$ films at 800 ºC. The bulk resistivity determined for the $TiSi_2$ annealed at 800ºC agrees with value of 15 μΩ-cm reported in the literature. However, the bulk resistivity determined for the $TiSi_2$ annealed at 600ºC was 36.90 μΩ-cm whereas the reported value was 60 μΩ-cm.[1]

Voltage measurements taken at the edge of the $TiSi_2$ samples were twice as much the voltage measurements taken at the center because the electric field in the center was full and spherical while the electric field at the edge was cut in half due to the discontinuity of the $TiSi_2$ samples. [2]

Table 3 summarizes the parameters used in the calculations of resistive and sheet resistance for the as deposited and annealed TiN films. The average resistivity measured at the center of the as deposited and annealed TiN samples were determined to be 16.805 μΩ-cm and 14.990 μΩ-cm, respectively. Correspondingly, the average sheet resistance for the as deposited and annealed TiN were calculated to to be 0.8402 Ω/sq and 0.7495 Ω/sq, respectively. It was observed that the deposited sample that underwent an annealing treatment showed lower resistivity and sheet resistance than the as deposited sample.

Table 3 : Resistivity Measurements for the as deposited and annealed TiN films with a thickness of 1.5×10^{-5} cm and current applied at the center.

TiN Sample	I (mA)	Forward Voltage (mV)	Reverse Voltage (mV)	Average Voltage (mV)	Sheet Resistance (Ω/sq)	Resistivity (Ω-cm)
As deposited	10	1.842	1.841	1.841	0.8345	1.669×10^{-5}
	60	11.20	11.20	11.20	0.8459	1.692×10^{-5}
Annealed	10	1.629	1.628	1.628	0.7381	1.476×10^{-5}
	60	10.07	10.07	10.07	0.7609	1.522×10^{-5}

After heat treatment, results show that the annealing process induces changes in lattice constant, grain size and resistivity in TiN films. [2] The manner of resistivity is in agreement with the recorded values in literature. They both showed similar trends. However, the resistivity for as-disposed and annealed TiN was recorded in the literature to be 73.3 μΩ-cm and 55 μΩ-cm, respectively. [3] The variance can be explained by the difference in sample thickness, the preparation method.

In all the samples, the silicon substrate was expected to increase the measurement of resistivity. This phenomenon can be explained by the fact that the electrical donors in p-type silicon increase the resistivity of the wafer. [2] Thermal EMFs were not significant since the voltage measurements were in the millivolt range. A thermal EMF is defined as a very small voltage in the microvolt range (μV) which is produced due to temperature variations across the resistor. [2] Nevertheless, when dealing with voltage measurements near the microvolt range, it is essentially critical to consider how the existence of thermal EMFs can greatly influence the accuracy of measurements.

Conclusion

The objective of this experiment was to use the four-point probe technique to correlate how the annealing treatment and crystal structures affect resistivity and sheer resistance. Using S-301 SIGNATONE for the four-point probe contacts, KETHLEY 2000 MULTIMETER for voltage measurements and HP 6181C DC CURRENT SOURCE for a constant current supply, two titanium silicide films, one annealed at 600 °C and one annealed at 800 °C, and two ceramic TiN films, one as deposited and one annealed, were examined.

Overall, the experiment was successful in showing how resistivity measurements depend on the different crystal structure resulted from different maximum annealing temperatures. The average resistivity measured at the center of the $TiSi_2$ samples annealed at 600ºC and 800 ºC were determined to be 36.96 μΩ-cm and 15.58 μΩ-cm, respectively. Furthermore, the average resistivity measured at the center of the as deposited and annealed TiN samples were determined to be 16.805 μΩ-cm and 14.990 μΩ-cm, respectively. It was concluded that the increase of annealing temperature results in changes in lattice constant and in lower defect density, vacancies or interstitials in $TiSi_2$ thin films which leads to decreasing in electrical resistivity. It was found that the as-deposited film showed higher electrical resistivity than the annealed sample. The experiment implies that the electrical properties can be improved by utilizing the annealing process as an added post-deposition treatment to enhance the microstructure and reduce the stresses and defects in the deposited films. Measurement precision was affected by many factors. Source of errors includes use of old samples that had may cracks and defects, poor contacts, noneuniformity of the sample thickness and composition. [1]

References

[1]L. Reynolds, Four Point Probe Experiment, MSE 335 experiment description, 2016.

[2] W.D. Callister Jr., Materials Science and Engineering: An Introduction, Seventh Edition (Wiley, New York, 2007).

[3] M. Popovic, M. Novakovic, and N. Bibic, Annealing effects on the properties of TiN thin films, Processing and Application of Ceramics PAC 9, 67 (2015).