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ELECTRICAL PROPERTIES OF POLYMER-DERIVED SILICOALUMINUM CARBOXIDE CERAMICS AND THEIR APPLICATIONS IN MICRO-SENSORS

by

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Major Professor: Linan An
ABSTRACT

Polymer-derived ceramic (PDC) is a new kind of material which is directly synthesized by the thermal decomposition of polymer precursors. Due to their unique structure, which consists of the amorphous matrix phase and free-carbon phase, PDCs exhibit many distinguished properties even at high-temperature environment such as oxidation and creep resistance, amorphous semiconducting behavior as well as piezoresistive behavior. These outstanding properties make PDCs become promising candidates for various applications especially for high-temperature microsensors.

However, most common used PDCs in the market now are SiC, SiCN and Si(M)CN ceramics, the high price and toxicity of their raw materials as well as strict operating requirements limit their applications. SiCO ceramics are appealing increasing attentions because they can cover these shortcomings of non-oxide ceramics, but their oxidation and corrosion resistance is so weak. In this dissertation, SiAlCO ceramics are chosen as main material. The addition of Al can improve the oxidation and corrosion resistance of SiCO ceramics.

In this dissertation, the SiAlCO ceramics are synthesized by using silicone resin and aluminum tri-sec-butoxide (ATSB), then ceramic samples are obtained by pyrolyzing disk green bodies at 1000, 1100, 1200, 1300, 1400°C.

Firstly, the composition, microstructure and structure evolution of SiAlCO ceramics are characterized via X-Ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Impedance spectroscopy (IS). The results indicate all ceramic samples
pyrolyzed below 1400°C are amorphous and a sudden structure change point around 1100°C is observed due to the increase of degree of ordering. Si-C, Si-O, C-C/H, and C=C bonds are observed within the materials.

Secondly, the room-temperature and temperature-dependent conductivity of the SiAlCO ceramics are studied. The optical absorption spectra are also measured. The conductivity increases by ~6 orders of magnitude when pyrolysis temperature increases from 1000 to 1400°C. A very high activation energy of 7.15eV is observed, and the redistribution of oxygen within the material is found to be responsible for it. Amorphous semiconductor behavior which follows the band-tail hopping (BTH) process is observed within this material. And the BTH process is resulted from unique electronic structures of the materials.

Thirdly, SiAlCO ceramic exhibits extraordinary piezoresistive behavior with an extremely high gauge factor in range of 7000 ~16000, which is higher than that of any previously reported high-temperature materials. The coupling effect of pressure and temperature on the piezoresistive behavior is also studied. The piezoresistive stress coefficient increases with increasing temperature, which is contradictive to other reported materials. Such change of the piezoresistive stress coefficient is due to the change in the characteristic temperature, which is reversely related to the density of state within the band-tail level.

In addition, SiAlCO also shows anomalous piezo-dielectricity with the positive pressure coefficient of the dielectric constant as high as 0.10-0.25 MPa⁻¹, which is much higher than that of other high-temperature materials. The polarizability of the material also increases with increasing pressure. These behaviors are attributed to the unique cell-like structure of the materials.
In the end, a pressure sensor is successfully developed. A supportive circuit is designed and the relationships among pressure, resistance and output voltage of the system are tested. The sensitivity of the sensor is calculated to be $\Delta V = 15.125$ Pa, indicating the SiAlCO ceramics are promising candidates for pressure sensor materials.
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LIST OF ACRONYMS/ABBREVIATIONS

ATSB  Aluminum Tri-sec-butoxide
BTH   Band-tail Hopping
EPR   Electron Paramagnetic Resonance
FTIR  Fourier Transform Infrared Spectroscopy
IS    Impedance Spectroscopy
MEMS  Micro-electro-mechanical Systems
NMR   Nuclear Magnetic Resonance
PDC   Polymer Derived Ceramic
PIP   Polymer Infiltration Pyrolysis
RTD   Resistance Temperature Detectors
RTM   Resin Transfer Molding
TGA   Thermal Gravimetric Analysis
VRH   Variable Range Hopping
XPS   X-ray Photoelectron Spectroscopy
XRD   X-ray Diffraction
CHAPTER ONE: INTRODUCTION

1.1: Motivation and objectives

A sensor is a device which can detect changes and then provide corresponding output, it has been widely used in various fields such as medical and healthcare\(^1\), engineering\(^2\) and transportation\(^3\). With the rapid development of modern engineering, many advanced industries such as unclear power plant and coal gasification plant are worked under high-temperature and harsh environment. In order to improve efficiency, reduce pollution, improve safety, obtain critical data and control accident, high-temperature sensors become more and more important. However most high-temperature sensors in the market now are metal-based temperature sensors, optical-based non-contact sensors and high-temperature ceramic-base sensors, they all have their own limitations and shortcomings, which cannot keep both thermal and functional stability under high-temperature and harsh environment. Therefore, new materials are urgently needed.

In the past few decades, tremendous attentions were appealed to polymer-derived ceramics (PDCs). Polymer-derived ceramic (PDC) is a new kind of material which is directly synthesized by the thermal decomposition of polymer precursors. Due to their unique structure, which consists of the amorphous matrix phase and free-carbon phase, PDCs exhibit many distinguished properties such as oxidation and creep resistance in high-temperature\(^4\), excellent mechanical properties\(^5\) as well as piezoresistive behavior\(^6\). These outstanding properties make PDCs become promising candidates for various applications especially for high-temperature applications. But now, most attentions are given to the non-oxide PDCs such as SiC, SiCN, SiBCN and SiAlCN ceramics. Not
only the cost of their raw materials are expensive, but their operating requirements are also very strict since oxygen must be avoided. Therefore, some new kinds of PDCs are urgently needed.

SiCO ceramics are good substitution because of several reasons. Firstly, their raw materials are commercial available at low price, which reduces the economic cost for both laboratorial researches and manufactory fabrication. Secondly, due to the existence of large amount of oxygen within themselves, the requirements for operating and storage also become softer. Last but not the least, most polymer precursors for SiCO are silicone resins, which are non-toxic to human body and eco-environment. However, their oxidation and corrosion resistance are weak, and an effective method to solve this problem is to add Al into this PDC system. Therefore, polymer-derived SiAlCO ceramics are chosen as the main material in this dissertation.

Then the overall objectives for this dissertation are:

1. Understand their conduction mechanism;
2. Study their piezoresistive behavior;
3. Design and test a pressure sensor using SiAlCO ceramic.

1.2: Outline of dissertation

This dissertation is composed of following parts:

Chapter 2 is the literature review of the background of polymer-derived ceramics and their applications in sensors. Chapter 3 is the experiment section. Detailed experimental procedures and characterization results are included. In Chapter 4, room-temperature conductivity and microstructure evolution of SiAlCO are discussed. Further investigation of their AC-conductivity via complex impedance spectra is studied in Chapter 5. In Chapter 6, combining the temperature-
dependent conductivity and optical absorption measurement, the electronic structures of SiAlCO ceramics are obtained. Chapter 7 is the study of their piezoresistive behavior and the coupling effect of pressure and temperature on the electronic behavior is studied in Chapter 8. Chapter 9 is the study on the piezo-dielectricity behavior of the material. In Chapter 10, a pressure sensor using the SiAlCO ceramic is developed and tested. In the end in Chapter 11, general conclusions of this dissertation are given.
CHAPTER TWO: LITERATURE REVIEW

2.1: Polymer-derived ceramics

2.1.1: Introduction to PDCs

Polymer-derived ceramic (PDC) is a new class of advanced materials which is directly derived from the thermal decomposition of polymer precursors. As compared with conventional polycrystalline ceramics, PDCs have a unique structure which consists of amorphous matrix and free-carbon phase. The first production of non-oxide ceramics synthesized from molecular precursors was reported in early 1960s\textsuperscript{7,8}. Ten years later, the transformation from polysilazanes, polysiloxanes and polycarbosilanes to Si\textsubscript{3}N\textsubscript{4}/SiC ceramics were successfully achieved\textsuperscript{9,10,11}.

In the past decades, various kinds of PDCs have been successfully synthesized by using different polymer precursors. Due to the nature of polymer precursors, they can provide PDCs with a tailored chemical composition, which has significant effects on the structure and properties of PDCs. The structure of PDCs is rather unique and complex, it is X-ray amorphous on macroscopic, but with heterogeneity in nanoscale. The most common used techniques for the characterization of the structure of PDCs are X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Electron paramagnetic resonance (EPR) as well as Nuclear magnetic resonance (NMR). Recently several new techniques such as DC-conductivity, optical absorption and Impedance spectroscopy (IS) have also been utilized to study the structures of PDCs.

Because of their unique and complex structure, PDCs not only show some outstanding general properties such as high strength, low density, high temperature shock resistance and high
oxidation/corrosion resistance, they also exhibit some unique structure-related properties such as high thermal stability to crystallization and decomposition, high creep resistance, high-temperature semiconducting, high piezoresistivity, large-range conductivity as well as temperature-dependent permittivity. These unique functional properties make PDCs become promising candidates for future applications.

Compared with conventional powder route which requires the sintering additives, the appearance of PDCs simplifies the whole process and provides more products options. For instance, with the help of polymer to ceramic transformation, ceramic fibers, layers or composite materials, which are rather difficult to obtain via conventional powder route, can be easily fabricated. In addition, several novel forming or shaping methods can be applied to preceramic such as polymer infiltration pyrolysis, injection molding, coating from solvent, extrusion or resin transfer molding\textsuperscript{12}. Once formed, the final ceramic products can be obtained by pyrolyzing the preceramic at high temperature and convert it to ceramic.

The basic processing procedures of PDCs are illustrated in Figure 1, which include:

1. Chemical synthesis of raw materials to obtain polymer precursor;
2. Cross-linking of polymer precursor to form infusible preceramic network;
3. Pyrolysis of preceramic network at 800-1000°C to get amorphous ceramic.

![Figure 1: The processing procedure of PDCs.](image-url)
2.1.2: Polymer precursors

PDCs are derived from polymer precursors, their chemical and physical properties can be heavily affected by the design of the molecular precursors; thus the synthesis of polymer precursors is a key point for PDCs. According to Birot\textsuperscript{13}, an ideal polymer precursor should have a compromise of following properties:

1. Sufficiently high molecular weight to avoid volatilization of oligomers;
2. Cages or rings structures should be included to reduce the elimination of volatile fragments due to backbone cleavage;
3. Certain degree of viscosity to ensure flexible shaping before the pyrolysis process;
4. Potential ability to acquire thermosetting or curing properties;
5. Low content of organic groups to increase ceramic yield and decrease unwanted free-carbon.

In recent years, most attentions are given to the silicon-based PDCs. The formula of organosilicon polymers is able to be simplified as shown in Figure 2\textsuperscript{12}. The backbone group X determines the classes of Si-based polymers, for instance, when X = Si, it’s poly(organosilanes); when X = CH\textsubscript{2}, it means poly(organocarosilanes), and when X = O, it’s poly(organosiloxanes). Figure 3 is a summary of current available precursors in the market\textsuperscript{12}. 
Figure 2: The molecular structure of the preceramic polymer\textsuperscript{12}.

\[
\begin{array}{c}
\text{R}^1 \\
\text{Si} \\
\text{R}^2 \\
\text{X}_n
\end{array}
\]

Figure 3: Different types of preceramic polymer precursors for Si-based ceramics\textsuperscript{12}.

Polysiloxanes are versatile materials because of their low price, excellent chemical, physical as well as electrical properties. The only disadvantage of siloxanes, the monomer of polysiloxanes, is they cannot be applied for the fabrication of fibers and films due to their low interactions between molecules. The structure of polysiloxanes are always modified by side chain functionalization or main chain modification to achieve new functions and optimize existing
properties. Such modification will lead to the change of the dimension of their macromolecular structure, such as ladder, sheet, cube and cage structures, and these structures have been found with characteristic thermal, optical, electrical and mechanical properties\textsuperscript{14}. Another efficient optimal method is to involve sila-functional oligosiloxanes to the synthesis process of polysiloxanes, but it’s not easy to be achieved.

Although tremendous organosilicon compounds are commercial available in the market, few products are available as reagent. Meanwhile, not only the price of these products are expensive, but there are also lots of limitations. Therefore, simple methods that can convert them to reliable precursors are expected.

Using Bifunctional silanes as starting materials, polysiloxanes with different structures can be obtained by synthesized under different conditions. For example, liner and cyclic structure are always achieved via controlled hydrolytic polycondensations with acid or base catalysis. Acid-catalysis tends to provide liner and branched polysiloxanes, and base catalyst and template prefers to form cube and pseudo-ladder silsesquioxanes as showed in Figure 4. And the detailed siloxanes bond formation reactions are illustrated in Figure 5. Besides, sol–gel reactions of sila-functional silanes are also an effective method to synthesis those materials mentioned above\textsuperscript{14}. 


Figure 4: The simple synthesis route for silica-based precursors\textsuperscript{14}.

Figure 5: Reactions for the siloxanes bond formation\textsuperscript{14}.
2.1.3: Processing of preceramic polymers

2.1.3.1: Shaping

For conventional ceramics, the selection of shaping process depends on the shape and size of the final products, as well as the microstructure demands. The most common used shaping methods include dry pressing, plastic forming, slip casting as well as pressure casting\textsuperscript{15}.

However these shaping processes have their own limitations. Pressing process is easy and inexpensive, but it can only be applied to simply shaped parts. If the shape of the parts are complex, the friction of the particles during pressing will finally lead to the uncontrolled shrinkage and cracks. Plastic forming is suitable for complex shaped parts, but the costs of the feedstock and mold are not cheap, not to mention the inflexibility. Although slip casting can highly control the homogeneities of the ceramic powders and provide products with increased properties and reliability, their porous molds are still not the best choice for the fabrication of nonporous microcomponents\textsuperscript{16, 17}.

For PDCs, due to their polymeric nature at processing temperature, they do not have drying problem, therefore large amounts of shaping methods can be applied to polymer precursors and some of those are even better than conventional ceramic shaping methods. The most common shaping methods for preceramic polymers applied in recent years include casting, impregnation/infiltration, coating, pressing, injection and extrusion.

2.1.3.2: Crosslinking

According to Colombo, a polymer precursor should be “a cross-linkable liquid, a meltable and curable solid or an unmeltable but soluble solid”\textsuperscript{12}. In order to ensure the processing parts can
retain their shape during the ceramization process, polymer precursors must be converted into thermoset via crosslinking. Crosslinking means the tight connections between polymer chains and it can be achieved by curing. The most common curing methods consists of thermal curing\(^\text{18}\), laser curing\(^\text{19}\), UV curing\(^\text{20}\) as well as curving under reactive gases\(^\text{21}\) and highly alkaline solution\(^\text{22}\). The selection of curing methods is depended on the properties of polymer precursors and products requirements. The curing temperature for thermal curing is usually below 200\(^\circ\)C, and can be lowered by adding catalysts. Sometimes during the thermal curing process, bubbles can be easily formed. With the introducing of catalysts, bubble formation can be inhibited\(^\text{23}\) and using overpressure medium can eliminate the bubble formation as well\(^\text{5}\).

2.1.3.3: Conversion from polymer precursor to ceramics

After shaping and crosslinking, the final step is to convert the preceramic network into ceramic via several processes such as thermal pyrolysis\(^\text{24}\), hot pressing\(^\text{25}\), spark plasma sintering\(^\text{26}\), chemical vapor\(^\text{27}\), laser pyrolysis\(^\text{28}\) and so on. Among these processes, thermal pyrolysis in a tube furnace with flowing gas is the most widely used one. During the conversion, some organic moieties such as methyl, Si-OH, Si-NH\(_x\) groups will be decomposed or eliminated\(^\text{12}\).

The thermal decomposition behavior of silica-based polymers is illustrated in Figure 6\(^\text{12}\). Based on different polymer precursors, different amorphous ceramics can be formed. As mentioned previously, the composition of these products can be tailored by changing the composition of polymer precursors. Combing thermal gravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR), quantitative analysis of the decomposition process can be obtained.
2.1.4: Microstructure of PDCs and characterization techniques

2.1.4.1: Microstructure of PDCs

The structures of amorphous PDCs are unique but complex, and will undergo different microstructural changes when pyrolysis temperature is higher than 1000 °C. Thus until now, clear explanations have not be stated. Previous researches demonstrated that most PDCs consist of amorphous matrix, disordered free-carbon as well as a certain amount of carbon dangling bonds as shown in Figure 7.
When the pyrolysis temperature increases, PDCs will transfer from amorphous state to partially crystalline state, and the structure evolution of PDCs could be summarized into three stages:\(^\text{12}\):

1: Phase separation during pyrolysis;

2: Graphitization process of the free-carbon phase;

3: Formation of nanocrystals.

2.1.4.2: Characterization techniques

2.1.4.2.1: X-ray diffraction (XRD)

X-ray diffraction is an effective technique to detect the crystallite sizes of different phases within PDCs. But due to the 1~2 vol% limitation, it is impossible to detect the first nanocrystals starting point. Figure 8 is a typical XRD pattern for SiCO and SiAlCO ceramics with different pyrolysis temperatures\(^\text{29}\). For SiCO samples, they are amorphous below 1200\(^\circ\)C since no peaks are observed, and at 1300\(^\circ\)C, both β-SiC and amorphous SiO\(_2\) are present. When the temperature
is up to 1400°C, the amorphous phase disappears. For SiAICO samples, their amorphous phase can be kept until 1300°C. When the temperature reaches to 1400°C, mullite begins to crystallize and amorphous SiO₂ can also be observed. Even though the XRD pattern is featureless at relative low temperature ranges, they still contain short-range structure features named nanodomains, which plays an important role in the resistance of PDCs to crystallization at high temperatures³⁰.

In addition, XRD also provides the opportunity to detect the in-plane crystallite size \( L_a \), crystallite thickness \( L_c \) and stacking for all types of carbon phases³¹.

![XRD patterns](image)

**Figure 8:** The XRD patterns of SiCO (a) and SiAlCO (b) ceramics pyrolyzed at different temperatures²⁹.

2.1.4.2.2: Raman spectroscopy

Raman spectroscopy is a useful spectroscopic method to observe vibrational, rotational, and other low-frequency modes in a system. For amorphous PDCs, Raman spectroscopy can indicate the existence of graphene sheets of carbon, but it cannot characterize the carbon bonds
because under amorphous state most bonds are overlapped. Since laser beam can only focus on micro scale areas, it is necessary to detect several areas and use the average signal.

Raman spectroscopy can also be used to detect the free-carbon phase within PDCs. For amorphous PDCs, their Raman spectra should contain two typical features of free-carbon phase: “D- and D’ peaks” at 1350 and 1620 cm⁻¹ due to the breathing mode of sp² carbon in ring, and “G- and G’ peaks” at approximately 1600 cm⁻¹ due to in-plane bond stretching of sp² carbon. Figure 9 is a typical Raman Spectra of polymer-derived SiCN ceramics. Figure 9: A typical Raman Spectra of polymer-derived SiCN ceramic.

The free-carbon concentration in PDCs can be calculated via a simple Raman-spectroscopy-based quantitative method developed by Jiang et al., in which an external reference is introduced. The size of the free-carbon clusters $L_a$ can also be estimated according to Equation (1):

\[
\frac{I_D}{I_G} = \frac{C(\lambda)}{L_a}
\]
where \( I_D \) and \( I_G \) are the intensities of D peak and G peak, which are calculated from the integrated area under each peak; \( C(\lambda) \) is a constant that depends on the wavelength of the incident beam.

2.1.4.2.3: X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a technique that not only measures the chemical composition and empirical formula of a material, but also measures the chemical and electronic states of elements within a material.

For X-rays with specific wavelength, their photon energies are known. Therefore, the electron binding energy of each emitted electrons can be calculated via Equation (2)

\[
E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi)
\]  

where \( E_{\text{binding}} \) is the binding energy (BE) of the electron, \( E_{\text{photon}} \) is the energy of the X-ray photons being used, \( E_{\text{kinetic}} \) is the kinetic energy of the electron as measured by the instrument and \( \phi \) is the work function of the spectrometer (not the material).

Chemical bonds within PDCs can be well recognized according to their specific binding energies. For instance, Figure 10 is a typical X-ray photoelectron spectroscopy of a polymer-derived SiCBN ceramic prepared at 1800\(^\circ\)C\(^{39}\). All peaks with different binding energy can be assigned to corresponding chemical bonds, which is quite important for the study of PDCs. In Figure 10(a), the peaks at 102.1 and 100.58 eV on Si 2p spectrum are assigned to Si–N, and Si–, respectively, which is consistent with presence of the SiC and Si\(_3\)N\(_4\) crystalline phases\(^{40}\). The same assumption is applied to B 1s spectrum, as shown in Figure 10(b), the peaks at 190.48, 190.03 and 189.58 eV are assigned to the B–N bonds of h-BN. For C 1s binding energy as shown in Figure
10(c), the peaks at 283.97 and 284.7 eV are assigned to C-Si bond of SiC and the C-C bond of graphite\textsuperscript{40}. In terms of the N 1s spectrum, the peaks at 397.3 and 197.99 eV belong to the N-B and N-Si bonds, respectively.

![Figure 10](image)

**Figure 10:** X-ray photoelectron spectroscopy of polymer-derived SiC\textsubscript{B}N\textsubscript{C} ceramic prepared at 1800\degree C: (a) Si\textsubscript{2p}, (b) B\textsubscript{1s}, (c) C\textsubscript{1s}, (d) N\textsubscript{1s}\textsuperscript{39}.

2.1.4.2.4: Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance spectroscopy is an effective research technique. By taking advantage of the magnetic properties of certain atomic nuclei, it can determine the physical and chemical properties of atoms or molecules of the material. This technique relies on the phenomenon of nuclear magnetic resonance and can provide detailed information about the
structure, dynamics, reaction state, and chemical environment of molecules. Therefore, it has been applied to various research fields.

NMR spectroscopy is usually used to investigate the structures and structure evolution of PDCs, and it can also provide some other detailed information about the materials. Since most PDCs are silicon-based, $^{29}$Si magic-angle-spinning (MAS) and $^{13}$C cross-polarization (CP) MAS NMR spectroscopic are most often used. Chen$^{41}$ used $^{29}$Si MAS NMR spectra to study the structure of SiCN ceramics. Figure 11 is the $^{29}$Si MAS NMR spectra of SiCN ceramics. By using Lorentz fitting, the broad curve can be split into three curves centered at $\delta_{\text{iso}}$ around ~19, ~34 and ~50 ppm, and these peaks belong to SiC$_4$, SiCN$_3$ and SiN$_4$ units, respectively. Calculating the relative concentration of these three species and converted them into mole concentration. Plotting the obtained mole concentration as a function of annealing temperature, it is seen that the concentration of the SiCN$_3$ decreased and that of the SiC$_4$ and SiN$_4$ increased, and they all showed a linear relationship as shown in Figure 12. The ratio of Si–C bonds to Si–N bonds was also calculated, and it remained constant indicating there was no net exchange between the Si-containing phase and the free carbon phase.
Figure 11: (a) $^{29}$Si solid-state NMR spectra of the SiCN pyrolyzed at different temperatures; and (b) curve fitting of $^{29}$Si NMR for the SiCN ceramic pyrolyzed at $1300^\circ\text{C}$\textsuperscript{41}. 

Figure 12: The mole percentages of different silicon bonding environments of the SiCN ceramics pyrolyzed at different temperatures$^{41}$. 

2.1.4.2.5: Optical absorption 

Optical absorption is a common method to study semiconductors. For an individual photon, if it has an energy which is higher than the semiconductor band gap, it can be absorbed and its energy will be transferred to an electron, then the electron can jump from the valence band into
the conduction band. For PDCs, they exhibit typical amorphous semiconductor behavior within certain photon energy range and their band gap and Tauc band gap can be estimated from their optical absorption spectra\textsuperscript{42}.

Recently, according to the study of Wang et al\textsuperscript{43}, combining conventional optical absorption spectra with temperature-dependent conductivity, analyzing the experimental results via theoretical models, the electronic structures of PDCs can be obtained. Figure 13 is the electronic structures of polymer-derived SiC ceramics pyrolyzed at different temperatures.

![Figure 13: Electronic structures of polymer-derived SiC ceramics pyrolyzed at different temperatures\textsuperscript{43}.](image)
2.1.5 Properties of PDCs

2.1.5.1: Thermal properties

PDCs have excellent thermal stability which makes them become promising candidates for high-temperature applications. Riedel\textsuperscript{44} synthesized a kind of polymer-derived SiBCN ceramic, and studied its thermal stability via relative mass loss versus temperature as shown in Figure 14. This SiBCN can withstand thermal degradation up to ~2000\textdegree{}C, which is much higher than the thermal degradation temperature of SiCN and Si\textsubscript{3}N\textsubscript{4}. The decomposition rate increases significantly when T\textgeq{}2100\textdegree{}C, and the rapid mass loss after 2100\textdegree{}C results from the evaporation of oxygen-containing species such as B\textsubscript{2}O\textsubscript{3}, SiO and CO\textsubscript{45}.

![Graph showing thermal gravimetric analysis of SiBCN, Si\textsubscript{3}N\textsubscript{4} and SiCN.]

**Figure 14: Thermal gravimetric analysis of SiBCN, Si\textsubscript{3}N\textsubscript{4} and SiCN\textsuperscript{45}.

The mass loss and composition of SiBCN annealed at 1000\textdegree{}C, 2000\textdegree{}C and 2100\textdegree{}C are summarized in Table 1\textsuperscript{45}. The composition of SiBCN annealed at 2000\textdegree{}C almost remains the same compared with the as-synthesized ceramic, revealing its excellent thermal stability. When
temperature reaches 2100°C, an obvious mass loss is observed, and the composition changes as well. This phenomenon consists with the results obtained from Figure 14.

### Table 1: The mass loss and chemical composition of SiBCN heat-treated at various temperatures under 0.1 MPa Ar

<table>
<thead>
<tr>
<th>Annealing temp. (°C) holding time (h)</th>
<th>Mass loss* (wt%)</th>
<th>Composition (wt%)</th>
<th>Total</th>
<th>Empirical formula†</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000/1</td>
<td>0</td>
<td>45.6</td>
<td>6.0</td>
<td>28.6</td>
</tr>
<tr>
<td>2,000/2</td>
<td>6</td>
<td>45.0</td>
<td>5.6</td>
<td>30.3</td>
</tr>
<tr>
<td>2,100/0.5</td>
<td>39</td>
<td>52.8</td>
<td>7.6</td>
<td>27.6</td>
</tr>
</tbody>
</table>

In Figure 15, XRD technique is used to analysis the crystallization resistance of SiBCN. SiBCN remains amorphous below 1700°C, and when annealing temperature reaches 2100°C, β-SiC is found as the only crystalline phase, indicating the excellent crystallization resistance.

**Figure 15:** The XRD results of SiBCN annealed at different temperatures
Except thermal stability, PDCs also exhibit excellent oxidation resistance and corrosion resistance. Wang\textsuperscript{46} reported a series of SiAlCN ceramics with different Al concentration and by measuring oxide-scale thickness as a function of oxidation time to study their oxidation kinetics. Their oxidation rate are summarized in Table 2. It is seen the oxidation rate of SiAlCN ceramics are much slower than that of pure SiCN and CVD SiC/Si\textsubscript{3}N\textsubscript{4}, indicating their excellent oxidation resistance.

Table 2: Oxidation rates of different silicon-based ceramics\textsuperscript{46}.

<table>
<thead>
<tr>
<th></th>
<th>$k_p \times 10^{18}$ (m\textsuperscript{2}/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCN</td>
<td>9.7</td>
</tr>
<tr>
<td>SiAlCN-10</td>
<td>1.2</td>
</tr>
<tr>
<td>SiAlCN-20</td>
<td>0.47</td>
</tr>
<tr>
<td>SiAlCN-30</td>
<td>1</td>
</tr>
<tr>
<td>CVD SiC [23]</td>
<td>16.4</td>
</tr>
<tr>
<td>CVD Si\textsubscript{3}N\textsubscript{4} [23]</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Wang\textsuperscript{47} also studied the corrosion resistance of SiAlCN ceramics by exposing them to pure water vapor flowing at the rate of 4.4 cm/s at 1100\textdegree C and analyzing their weight changes as a function of annealing time. The corrosion rate of different ceramics are listed in Table 3, showing SiAlCN ceramic also has the best corrosion resistance.
Table 3: Parabolic Rate Constants ($k_p$) and Linear Rate Constants ($k_l$) for Silicon Based Materials$^{47}$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$k_p \times 10^7$ (mg·(cm$^2$·h)$^{-1}$)</th>
<th>$k_l \times 10^4$ (mg·(cm$^4$·h)$^{-1}$)</th>
<th>Experimental condition</th>
<th>Temperature (°C)</th>
<th>$Q$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCN</td>
<td>3.7$^T$</td>
<td>38.2</td>
<td>100% water vapor, flowing rate: 4.4 cm/s</td>
<td>1100</td>
<td>—</td>
</tr>
<tr>
<td>SiAlCN</td>
<td>0.96$^T$</td>
<td>5.5</td>
<td>100% water vapor, flowing rate: 4.4 cm/s</td>
<td>1100</td>
<td>—</td>
</tr>
<tr>
<td>CVD SiC</td>
<td>8.5$^T$</td>
<td>—</td>
<td>50% H$_2$O–50% O$_2$, flowing rate: 4.4 cm/s</td>
<td>1200–1400</td>
<td>35±147</td>
</tr>
<tr>
<td>CVD Si$_3$N$_4$</td>
<td>14.8$^T$</td>
<td>—</td>
<td>50% H$_2$O–50% O$_2$, flowing rate: 4.4 cm/s</td>
<td>1200–1400</td>
<td>21±51</td>
</tr>
</tbody>
</table>

$^T$k at 1100°C in 100% water vapor of flowing rate of 4.4 cm/s.

Figure 16 are the surface and cross-section SEM images of SiCN and SiAlCN ceramics after annealing for 100h. It is obvious Al-modified SiCN shows smoother surface and cross-section than that of pure SiCN, indicating its excellent resistance to water vapor corrosion.

![Figure 16: SEM images of the surface and cross-section of polymer-derived SiCN and SiAlCN after annealing for 100 h$^{47}$.](image-url)
2.1.5.2: Mechanical properties

Mechanical properties are also important index for the applications of PDCs. Table 4 is some selected properties of SiCO-based ceramics in comparison with quartz glass. It is seen polymer-derived SiCO-based ceramics have a higher Vicker’s hardness and elastic modulus, and their glass transition temperature is also higher than that of pure silica, indicating a wider application temperature range.

**Table 4: Some selected properties of SiCO-Based Ceramics in comparison with Quartz Glass (pure Silica)**

<table>
<thead>
<tr>
<th>Property</th>
<th>SiCO Glass</th>
<th>Silica</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vicker’s Hardness</td>
<td>8-9 GPa</td>
<td>6-7 GPa</td>
<td>200-1000 g load</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>97.9 GPa</td>
<td>70 GPa</td>
<td>Vibration method</td>
</tr>
<tr>
<td>Glass transition</td>
<td>1350°C</td>
<td>1190°C</td>
<td>Viscosity: $10^{13}$ Pa·s</td>
</tr>
</tbody>
</table>

Some mechanical and thermal properties of selected polymer-derived ceramic fibers and bulk materials are also listed in Table 5 and Table 6. All the polymer-derived samples exhibit excellent mechanical properties.
Table 5: Tensile strength, Elastic modulus and Density of Polymer-derived Ceramic Fibers\textsuperscript{12}.

<table>
<thead>
<tr>
<th>System</th>
<th>Precursor</th>
<th>Tensile strength, $\sigma_T$ (GPa)</th>
<th>Elastic Modulus, $E$ (GPa)</th>
<th>Density, $\rho$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(O)C</td>
<td>Polycarbosilane</td>
<td>3</td>
<td>200</td>
<td>2.55</td>
</tr>
<tr>
<td>SiC</td>
<td>Polycarbosilane</td>
<td>2.5</td>
<td>400</td>
<td>3.05</td>
</tr>
<tr>
<td>Si–Ti–C–O</td>
<td>Polytitanocarbosilane</td>
<td>3</td>
<td>220</td>
<td>2.35</td>
</tr>
<tr>
<td>Si–Al–C–O</td>
<td>Polyaluminocarbosilane</td>
<td>3</td>
<td>300</td>
<td>3.0</td>
</tr>
<tr>
<td>Si–B–C–N</td>
<td>B-modified polysilazane</td>
<td>1.3</td>
<td>170</td>
<td>1.95</td>
</tr>
<tr>
<td>BN</td>
<td>Poly[(methylamino)borazine]</td>
<td>1.48</td>
<td>365</td>
<td>2.6</td>
</tr>
<tr>
<td>Si–Al–O–N</td>
<td>Polyaluminocarbosilane</td>
<td>1.75</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 6: Summary of the Mechanical and Thermal Properties Measured on Bulk Samples of the SiCN and SiCO Systems\textsuperscript{12}.

<table>
<thead>
<tr>
<th>System</th>
<th>Bulk density, $\rho$ (g/cm$^3$)</th>
<th>Elastic modulus, $E$ (GPa)</th>
<th>Vickers hardness, HV (GPa)</th>
<th>Fracture strength, $\sigma_T$ (MPa)</th>
<th>Fracture toughness, $K_{IC}$ (MPa m$^{1/2}$)</th>
<th>Thermal expansion, $\alpha$ ($\times 10^6$°C$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCN (Ceraset)</td>
<td>1.85–2.16</td>
<td>82–140</td>
<td>8.3–11.3</td>
<td>$&lt;1000$</td>
<td>0.21–0.24</td>
<td>0.56–1.3</td>
</tr>
<tr>
<td>SiCN(NCP200)</td>
<td>2.3</td>
<td>155</td>
<td>15–26</td>
<td>$&lt;118$</td>
<td>0.21–0.24</td>
<td>2–3</td>
</tr>
<tr>
<td>SiC (VT30)</td>
<td>1.95</td>
<td>105</td>
<td>6.1</td>
<td>88–146</td>
<td>2.1</td>
<td>3.08–3.96</td>
</tr>
<tr>
<td>SiCN (HVNG/HPS)</td>
<td>2.6</td>
<td>109–118</td>
<td>7.9–12.8</td>
<td>$&lt;118$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Si(O)C (AHPCS)</td>
<td>2.3–2.9</td>
<td>9–13</td>
<td>6.4</td>
<td>80–235</td>
<td>2.1</td>
<td>3.08–3.96</td>
</tr>
<tr>
<td>SiCO (sol–gel)</td>
<td>1.7–2.28</td>
<td>57–113</td>
<td>4.7–9.3</td>
<td>70–900</td>
<td>0.57–0.77</td>
<td>3.21</td>
</tr>
<tr>
<td>SiOC (MK)</td>
<td>2.23</td>
<td>101</td>
<td>6.4</td>
<td>0.11</td>
<td>1.8</td>
<td>3.14</td>
</tr>
<tr>
<td>SiOC (SR350)</td>
<td>2.35</td>
<td>97.9</td>
<td>8.5</td>
<td>133–612</td>
<td>1.8</td>
<td>3.14</td>
</tr>
</tbody>
</table>

2.1.5.3: Electrical properties

Except excellent thermal and mechanical properties, PDCs also have many unique and outstanding electrical properties, which makes them become distinguished functional materials, especially for sensor applications. In this dissertation, only conductivity, impedance and piezo-resistivity will be discussed.
2.1.5.3.1: Conductivity

As previously mentioned, PDCs are composed of amorphous matrix and free carbon phase. An\textsuperscript{49} concluded the possible conducting mechanisms according to their microstructure and drawn in Figure 17. When the free carbon phase is isolated, a critical concentration is introduced. If the free carbon concentration is higher than the critical value, the electrical conductivity of the material follows percolation models; if the carbon concentration is lower than the critical value, amorphous matrix is dominant for the electrical conductivity and showing a typical amorphous semiconductor behavior.

![Figure 17: Schematic showing the possible conduction mechanisms in polymer-derived ceramics\textsuperscript{49}.](image)

2.1.5.3.1.1: DC-conductivity

Figure 18\textsuperscript{50} is the DC-conductivity of SiCN ceramics as a function of annealing time and annealing temperature. $T_0$ describes the temperature dependence of $\sigma_{d.c.}$ according to Equation (6).
Then the change of electrical conductivity can be related to three temperature regimes which corresponds to the microstructure changes\textsuperscript{51}.

\[ \sigma_{d.c.} \propto e^{-\frac{T_0}{T}} \]  \hspace{1cm} (3)

In regime I ($1000^\circ C < T_a < 1400^\circ C$), with the increase of annealing temperature, conductivity $\sigma_{d.c}$ increases and $T_0$ decreases. Such changes are due to the loss of hydrogen, which finally leads to the structure change of Si-C-N phase, decreasing the overall energy barrier.

In regime II ($T_a > 1400^\circ C$), the conductivity increases sharply and the isothermal annealing time $t_a$ also has a significant effect on it. The change in the conductivity is due to the formation of nano-crystalline SiC and the reduction of the N-content in the amorphous matrix.

In regime III ($T_a > 1400^\circ C$), no sp$^2$ carbon can be measured, and the conductivity is equal to that of crystallized SiC\textsuperscript{50,52}.
2.1.5.3.1.2: AC-conductivity

Figure 19 is the plot of the real part $\sigma'$ of the conductivity as a function of the annealing conditions, and it show a typical semiconductor behavior. At high frequency, $\sigma_{a.c.}$ is generated by small-distance separated states, however at lower frequency, large-distance separated states leads to the appearance of $\sigma_{a.c.}$. When testing frequency is infinitely near zero, $\sigma_{a.c.}$ equals to $\sigma_{d.c.}$. Annealing temperature also has effect on the ac-conductivity. When annealing temperature reaches 1300$^0$C, $\sigma_{d.c.}$ is dominant.
2.1.5.3.2: Piezoresistivity

Recently, a new discovery has been reported that PDCs exhibit excellent piezo-resistive behavior, which means the resistivity of PDCs changes with the applied stress. Zhang\textsuperscript{53} reported the piezoresistive behavior of SiCN ceramic, and this material showed a high gauge factor along both longitudinal and transverse ranging from 1000~4000, which was higher than any existing ceramics. Previous study demonstrated the existence of graphene sheets within PDCs, and the applied stress could slightly decrease the distance between the graphene sheets, leading to the change of resistivity. And they also concluded this piezoresistive behavior followed the tunneling-percolation model\textsuperscript{54}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure19.png}
\caption{Plot of the real part $\sigma'$ of the conductivity as a function of the annealing conditions\textsuperscript{50}.}
\end{figure}
Riedel et al\textsuperscript{6} also reported the piezoresistive behavior of SiOC ceramics annealed at 1400\textdegree C, the gauge factor calculated from their experimental data equaled to \( \sim 145 \) and the pressure change of \( \Delta \sigma \approx 8 \text{MPa} \) leaded to a change in the resistivity of \( \Delta R \approx 35 \Omega \). But it is interesting that for this materials, the resistivity increased with the increasing applied stress, which was opposite to that of SiCN ceramics as reported by Zhang.

Figure 20: Plot of gauge factors as a function of the applied pressure for (a) longitudinal and (b) transverse directions.

Figure 21: The piezoresistive response in the SiCO ceramic annealed at 1400\textdegree C via monitoring of the electrical resistance and the applied mechanical pressure versus time\textsuperscript{6}.
2.2 Background of sensors and PDC-based high-temperature sensors

A sensor is a useful device which detects events or changes in its environment and then provides a corresponding output. It can be used to detect different parameters such as temperature, pressure, gas, ultrasonic and so on. Meanwhile, sensors may provide various types of output, but electrical and optical signals are the most common ones.

The development of sensors used in normal temperature range environment is relative mature and those sensors have been successfully applied in various aspects of human life such as temperature/humanity monitor, cellphone, autos and so on. However sensors used in high-temperature harsh environment such as turbine engines, nuclear reactors as well as coal gasification are still urgently needed. With the help of a suitable sensor, not only the efficiency and safety can be improved, but the maintenance cost can also be reduced.

There are three main kinds of high-temperature sensors in the market now, metal-based sensors, optical-based sensors as well as high-temperature ceramic based sensors. Metal-based sensors such as resistance temperature detector (RTD) is always made from a pure material, typically platinum, nickel or copper. The resistance of these materials can be varied with temperature change, which can be used to determine temperature. But due to the nature of pure metal, they are easily got severe oxidation and degradation, limiting their lifecycle time. Optical-based sensors such as optical pyrometer is a device which can detect the temperature of a surface from the spectrum of the thermal radiation it emits from a certain distance. By selecting different based materials such as rare earth oxide, the detecting temperature range has been increased to >1500°C, but their accuracy and repeatability still need to be improved. High-temperature
ceramic based sensors such as SiC capacitive pressure sensor\textsuperscript{56} is another common sensing technique. However due to its narrow sensing temperature range (<500\(^\circ\)C) and high fabrication cost, it has not been widely used.

Recently, PDCs are appealing tremendous attentions from high-temperature sensors fields because of their excellent thermal stability, mechanical properties and sensing functions. Several PDC-based sensors have been successfully developed.

2.2.1: PDC-based high-temperature pressure sensor

Recently, Cheng and co-workers\textsuperscript{57} successfully developed a wireless pressure sensor made of polymer-derived SiAlCN ceramic for high-temperature applications. The mechanism of this sensor is based on a microwave evanescent-mode cavity resonator. Meanwhile, by using integrated patch antenna, the sensor could had a compact size and higher sensing range. The schematic of this wireless pressure sensor was demonstrated in Figure 22.

![Figure 22: The schematic of the wireless pressure sensor\textsuperscript{57}.](image)
The pressure sensor was measured in a temperature range of 25–800°C under different forces up to 5N. The resonant frequency $f_r$ was measured and plotted in Figure 23 as a function of temperature and force. It is seen the resonant frequency $f_r$ decreases with increasing applied force in a linear relationship. However, the resonant frequency $f_r$ also decreases with increasing temperature, a temperature sensor is needed to calibrate the frequency drift due to the temperature effect.

![Plot of resonant frequency $f_r$ as a function of temperature and force.](image)

**Figure 23: Plot of resonant frequency $f_r$ as a function of temperature and force.**

Another polymer-derived SiOCN ceramic, which was potential pressure sensor material used for high-temperature environment, was reported by Terauds and colleagues\(^5\). Compressive loading ranging from 0 to 10MPa was applied to the sample for several cycles under each temperature point from 700°C to 1000°C and the resistance was calculated via its I-V curve. The resistance and gauge factor as a function of stress at different temperature were plotted in Figure 24. The outstanding repeatability and high gauge factor indicating this material was suitable for future high-temperature sensor applications.
2.2.2: PDC-based high-temperature temperature sensor

Recently, Zhao\textsuperscript{59} reported a temperature sensor using polymer-derived SiAlCN ceramic via a simple circuit as shown in Figure 25. By using this circuit, the change in resistance can be reflected by the change of output voltage ($V_s$) according to Equation (4):

$$V_s = \frac{R_s}{R_p + R_s} \cdot V_i$$  \hspace{1cm} (4)

The output voltage monotonically decreased with increasing temperature. Using Equation (5)

$$T_{sensor} = \frac{C_1}{C_2 + \ln \left( \frac{1}{R_s/R_i - R_s} \right)}$$  \hspace{1cm} (5)

where $C_1$ and $C_2$ are constants, the sensing temperature was obtained. The calculated sensing temperature showed a great consistence with the temperature measured from thermal couple as shown in Figure 26, demonstrating the accuracy of this sensor.
Figure 25: The circuit converting resistance output to voltage signal\textsuperscript{59}.

![Circuit Diagram]

Figure 26: Experimental comparison between the PDC measurement with the thermal couple measurement\textsuperscript{59}.

![Graphs]

2.3 Amorphous semiconductor model and conduction mechanism

Figure 27 is the schema of a crystal model and a corresponding band model. The black triangles represent a short-range order. In this band model, the forbidden band (bandgap) $E_{\text{gap}}$ exists between the conduction and valence bands, and electrons and holes can transport between these two bands if they have efficient energy\textsuperscript{60}.

\[ \text{Time (Min)} \]
\[ \begin{array}{c|c}
0 & 50 & 100 & 150 & 200 & 250 \\
\hline
\text{Output voltage $V_{s}$ (Volt)} & 4.1 & 3.9 & 3.7 & 3.5 & 3.3 \\
\text{Temperature from PDC $T_{\text{sensor}}$ (°C)} & 680 & 690 & 700 & 710 & 720 \\
\text{Temperature from thermal couple $T$ (°C)} & 680 & 690 & 700 & 710 & 720 \\
\end{array} \]
Figure 27: A crystal model and a corresponding band model model of the crystal\textsuperscript{60}.

The model for amorphous semiconductors are more complex. Amorphous semiconductors are widely used in electronic devices\textsuperscript{61}, understanding their mechanism is quite important for future improvement. Several models had been developed to investigate their electrical properties such as Cohen, Fritzsche and Ovshinsky (1969), which is illustrated in Figure 28 and followed by Gubanov (1963) and Banyai (1964). They believed that the valence and conduction bands in amorphous semiconductors have “tails” of localized states and those “tails” can overlap, so that the density of states at the Fermi level is finite\textsuperscript{62}. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure27.png}
\caption{A crystal model and a corresponding band model model of the crystal.}
\end{figure}
Figure 28: Density of states in an amorphous semiconductor alloy according to Cohen et al.1969. Localized states are shown shaded.

However, according to David and Mott, those models should be modified by introducing a band of localized state near the center of the gap as demonstrated in Figure 29. In Figure 29, energies denoted by $E_V$ and $E_C$ constitute the borders between localized and extended states and correspond to the mobility edges. The distance between them is called mobility gap $E_g$, which is equivalent to the bandgap for crystalline materials. The distance $E_AE_B$ is called the optical gap $E_O$, determined by the optical absorption edge. $E_F$ is the Fermi level energy. In this model, electrons and holes can transport via the extended states or by a hopping mechanism via the localized states. David and Mott distinguished that (i) the ranges $\Delta E_C$, between $E_C$ and $E_A$, and $\Delta E_V$, between $E_B$ and $E_V$, where the localized states lie in the bands and are due to the lack of long-range order, and (ii) hypothetical “tails” due to defects in the structure.

In perfect amorphous materials, the difference between $E_g$ and $E_O$ is only a few tenths of an electron volt which is due to the lack of long-range order. However real amorphous materials
contain numerous defects, these defects will finally fill the gap out either partly or even completely due to the formation of additional localized states within the mobility gap$^{60}$.

![Diagram](image)

**Figure 29:** Suggested density of states $N(E)$ and mobility $\mu$ as a function of energy in an amorphous semiconductor. Localized states are shown shaded.

According to Mott’s model, there are three conduction mechanisms for amorphous semiconductors: the conduction in extended states, the conduction in band tails, and the conduction in localized states. In high-temperature range, electrons jump from defect level to conduction band, and holes jump from valence band to defect level, it is the conduction in extended states. In middle-temperature range, electrons jump from defect level to band tail, and holes jump from band tail to defect level, it is the conduction in band-tail states. In low-temperature range, electrons jump near Fermi level following the variable range hopping (VRH) mechanism, it is the conduction in localized states. Later on, a revised model is reported as in low-temperature range, electrons firstly
jump from defect level to band tail, then jump back to Fermi level following the band tail hopping (BTH) mechanism.
CHAPTER THREE: SYNTHESIS OF AMORPHOUS SiALCO CERAMICS AND CHARACTERIZATION

3.1: Synthesis of amorphous SiAlCO ceramics

3.1.1: Raw materials

1. The polysiloxane used in this synthesis process is a commercial available silicon resin (SIRLES® H62 C, Wacker Chemical Corporation, Adrian, MI). It is a phenyl-containing poly(siloxane) of high carbon content (45.5wt%) and its chemical formula can be simplified as RSiO₁.₅, where R=\([(C₆H₅)₂₈(CH₃)₁₅(CH₂=CH),(H)]\).

2. Aluminum tri-sec-butoxide \((\text{C}_₄\text{H}_₉\text{O})_₃\text{Al}\), Sigma-Aldrich, St. Louis, MO) is the source of Al in this experiment, its molecular formula is drawn in Figure 30.

![Figure 30: Molecular Formula of ATSB.](image)

3.1.2: Synthesis procedures

Silicone resin is first mixed with ethanol in a mass ratio of 2:1; 5wt% of aluminum tri-sec-butoxide with respect to silicone resin is then added to the mixture. The mixture is stirred at 800 rmp for 6 hours at room temperature to ensure the completion of the reaction between the silicone and ATSB. The liquid mixture is solidified at 150°C for 18 hours in air and followed by a heat-treatment at 350°C for 4 hours under flowing ultrahigh purity argon. The fully cross-linked solids are ball milled and sieved to obtain particle of ~1μm. The powders are then compressed at a
uniaxial pressure of 20MPa followed by a cold isostatic pressure of 200MPa to form green bodies. SiAlCO ceramics are obtained by pyrolyzing the disk green bodies at 1000, 1100, 1200, 1300 and 1400°C for 4 hours in a tube furnace under flowing ultrahigh purity argon following the sintering procedures in Figure 31.

3.2: Characterization and results

3.2.1: Chemical composition

The chemical composition of the SiAlCO ceramic is determined by a combination of IR carbon-sulfur analyzer and oxygen-nitrogen analyzer (EMIA-320V/EMGA-620V, Horiba Co., Hakata-ku, Japan). The chemical composition of the sample is SiC_{0.93}O_{0.57}Al_{0.03}, and all samples almost have same chemical composition regardless of pyrolysis temperature.

3.2.2: X-ray diffraction

SiAlCO ceramics pyrolyzed at different temperatures are grinded to powder and their crystallization behavior are detected by Rigaku D/MAX X-ray Diffractometer (XRD Rigaku, Tokyo,

Figure 31: A schematic of the sintering procedures of SiAlCO.
Japan) with a monochromatic Cu-Kα radiation and a wavelength of 0.154nm. Figure 32 is the XRD pattern of SiAlCO ceramics pyrolyzed at different temperatures. It is seen that all samples are amorphous without detectable diffraction peak, except the sample pyrolyzed at 1400°C, which shows a very weak peak corresponding to SiC. The results suggest SiAlCO ceramics are highly stable against crystallization.

![XRD pattern of SiAlCO ceramics pyrolyzed at different temperatures.](image)

**Figure 32: XRD pattern of SiAlCO ceramics pyrolyzed at different temperatures.**

3.2.3: Raman spectroscopy

Raman spectra are obtained by using a Renishaw inVia Raman microscopy (Renishaw Inc., Gloucestershire, UK) with the 514nm line of silicone-solid laser as the excitation source. Since laser beam can only focus on micro scale areas, ten areas are detected and the average signal is used for analysis. Figure 33 is the Raman spectra of SiAlCO samples pyrolyzed at different temperatures. The spectra contain the typical features of free-carbon in polymer-derived ceramics:
D peak at ~1350 cm\(^{-1}\) due to the breathing modes of sp\(^2\) carbon atoms in rings and G peak at ~1600 cm\(^{-1}\) resulted from in-plane bond stretching of sp\(^2\) carbon.\(^{32, 38, 63, 64, 65}\)

**Figure 33:** Raman spectra of the SiAlCO samples pyrolyzed at different temperatures, as labeled.

### 3.2.4: X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is used to further analyze the free-carbon phase within the material. XPS is carried out on an AXIS ULTRA (Kratos) apparatus (PHI-5400, Perkin Elmer, Waltham, U.S.A), using monochromatic Al K\(\alpha\) radiation (hv=1486.6eV) at 150W. To remove possible contaminations, the surfaces of the samples are first etched by Ar+ ions for 10mins. The spectra are recorded at room temperature under high vacuum (10-9Torr). Figure 34 are the XPS spectra of the C1s electron state for the SiAlCO ceramic prepared at 1000, 1100, 1200 and 1300\(^\circ\)C. Taking the XPS spectrum of sample pyrolyzed at 1100\(^\circ\)C as example, the complex spectrum can be deconvoluted into four peaks, the peaks at 282.7eV, 284eV, 285eV and 286.5eV
are assigned to C-Si, C=C, C-C/H and C-O bonds as shown in Figure 35, respectively. The relative concentration of the four bonds can be estimated from the ratio of the integrated area under each peak and the results are listed in Table 7.

Figure 34: XPS spectra of the C1s electron state for the SiAlCO ceramic prepared at 1000, 1100, 1200 and 1300°C.
Figure 35: The XPS spectra of the C1s electron state for the SiAlCO ceramic prepared at 1100°C.

Table 7: Relative bond concentrations of the SiAlCO ceramics pyrolyzed at different temperatures.

<table>
<thead>
<tr>
<th>Pyrolysis Temperature(°C)</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O</td>
<td>10.45%</td>
<td>10.04%</td>
<td>10.85%</td>
<td>10.33%</td>
</tr>
<tr>
<td>C-Si</td>
<td>21.28%</td>
<td>21.79%</td>
<td>21.15%</td>
<td>21.39%</td>
</tr>
<tr>
<td>C=C</td>
<td>62.10%</td>
<td>63.22%</td>
<td>64.45%</td>
<td>65.83%</td>
</tr>
<tr>
<td>C-C/H</td>
<td>6.15%</td>
<td>4.93%</td>
<td>3.53%</td>
<td>2.42%</td>
</tr>
</tbody>
</table>
3.2.5: Conductivity

3.2.5.1: DC-conductivity at room temperature

To measure the electric conductivity, silver paste is painted on both sides of samples as electrodes. The room–temperature DC-conductivities of samples pyrolyzed at different temperatures are obtained by measuring their I-V curves on KEITHLEY 2400 (Keithley Instruments, Inc., Cleveland, OH) and listed in Table 8.

**Table 8: Room-temperature DC-conductivities of the SiAlCO ceramics pyrolyzed at different temperatures.**

<table>
<thead>
<tr>
<th>Pyrolysis Temperature(⁰C)</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
<th>1400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity(s/cm)</td>
<td>1.33E-7</td>
<td>4.99E-6</td>
<td>3.68E-4</td>
<td>1.90E-2</td>
<td>6.93E-1</td>
</tr>
</tbody>
</table>

3.2.5.2: DC-conductivity in high-temperature range

Silver paste is painted on both sides of samples as electrodes in order to measure their temperature-dependent conductivities. The temperature-dependent conductivities of samples pyrolyzed at different temperatures are measured in a tube furnace under flowing ultrahigh purity argon and a thermal couple is placed just above the samples to record the accurate testing temperatures. The DC-conductivities are obtained by measuring samples’ I-V curves on KEITHLEY 2400 (Keithley Instruments, Inc., Cleveland, OH) in the temperature range of 50-650⁰C. Figure 36 is the plot of the electric conductivity as a function of testing temperature.
3.2.6: Optical absorption

After the temperature-dependent conductivity measurement, all samples are grinded to powder of ~1um in order to maintain the accuracy and reliability of the optical absorption measurement. The powder are first mixed with KBr powder and then compressed into a disc of 10mm in diameter and 0.5mm in thickness. The ratio of the SiAlCO powder to the KBr powder is adjusted to ensure the overall absorption coefficient is between 0.2-0.8 for the optimal results. The optical absorption spectra are obtained on a UV-3101 double channel spectrometer (Shimadzu Co., Kyoto, Japan). Figure 37 is the plot of room-temperature optical absorption spectra for the amorphous SiAlCO pyrolyzed at different temperatures.
3.2.7: Impedance spectra

Silver paste is applied on both sides of the disk samples as electrode. The complex impedance ($Z^*$) spectra of the disk samples are measured on a LCR meter (Agilent 4980A, Agilent Technologies, Santa Clara, California, USA) in the frequency range of 20Hz to 2MHz. Figure 38 is the complex impedance spectra of SiAlCO samples pyrolyzed at different temperatures.
Figure 38: Complex Impedance Spectra of SiAlCO samples pyrolyzed at different temperatures.
CHAPTER FOUR: ELECTRIC CONDUCTIVITY AND MICROSTRUCTURE EVOLUTION OF SIALCO CERAMICS

4.1: Introduction

Electric conductivity is one of the basic electric properties of PDCs, which has been extensively studied. Several conduction mechanisms for PDCs have been proposed. If the free-carbon phase is continuous, the conduction of PDCs is dominated by the glassy carbon phase\textsuperscript{69}. If the free-carbon phase is isolated, two mechanisms are followed\textsuperscript{70}. When the free-carbon concentration is higher than a certain critical concentration, the conduction is controlled by a tunneling-percolation process; when the free-carbon concentration is lower than the critical concentration, the conduction mechanism is controlled by the Si-based amorphous matrix, following the amorphous semiconducting behavior. Previous studies showed that for polymer-derived SiCN ceramic, the increase in the electric conductivity with increasing pyrolysis temperature is due to the increase in conductivity of free-carbon phase\textsuperscript{71}. However for the acrylic acid-modified SiCN, the conduction mechanism could not be explained clearly\textsuperscript{72}. These phenomena suggest that the existence of oxygen highly affect the conductivity of the materials. Since a large amount of oxygen also exists in the SiAICO ceramic, its conduction behavior could be more complex.

In this chapter, the electric conductivity of the SiAICO ceramic samples pyrolyzed at different temperatures are studied. Related microstructure evolution of these samples are also investigated.
4.2: Experimental procedures

The synthesis procedures of samples have been illustrated in Chapter 3. DC-conductivity, Raman spectra and XPS results are used to analyze their electric conductivity and microstructure evolution.

4.3: Results and discussion

The measured DC-conductivities of the samples pyrolyzed at different temperatures are listed in Table 8. The conductivities increase by ~6 orders of magnitude when the pyrolysis temperature increases from 1000 to 1400°C, which is much larger than the conductivity change of SiCN and SiC ceramics reported previously. Figure 39 is the plot of the natural logarithm of conductivity \([\text{Ln}(\sigma)]\) versus the reciprocal of pyrolysis temperature \([1000/T]\), it shows the conductivity follows the Arrhenius law, according to Equation (6):

\[
\sigma = \sigma_0 \exp\left(-\frac{\mu}{kT}\right)
\]  

(6)

where \(\sigma\) is the conductivity of the SiAlCO ceramics, \(\mu\) is activation energy, \(T\) is pyrolysis temperature, \(k\) is Boltzmann constant and \(\sigma_0\) is a prefactor, the calculated activation energy \(\mu\) equals to 7.15eV. Previously, Chen\(^73\) et al has reported if the increase in conductivity is due to the free-carbon phase within the material, the activation energy obtained from the Arrhenius relation should be similar to that for the \(sp^3\)-to-\(sp^2\) transition of the free-carbon phase. The difference between activation energies suggests the increase in conductivity is not only dominated by the free-carbon phase.
Figure 39: Plot of natural logarithm of conductivity [Ln(σ)] as a function of the reciprocal of pyrolysis temperature [1000/T] for SiAlCO ceramics.

In order to have a better understanding of the conduction mechanism, Raman spectroscopy is carried out to analyze the structure of SiAlCO ceramics. The Raman spectra of SiAlCO samples pyrolyzed at different temperatures are shown in Figure 33. The spectra contain the typical features of free-carbon in polymer-derived ceramics: D peak at ~1350 cm\(^{-1}\) due to the breathing modes of \(sp^2\) carbon atoms in rings and G peak at ~1600 cm\(^{-1}\) resulting from in-plane bond stretching of \(sp^2\) carbon\(^{32, 38, 63, 64, 65}\). The Raman spectra are curve-fitted by using Lorentzian function for D peak and Breit–Wigner–Fano function for G peak\(^{74}\). The position and full width at half maximum (FWHM) are obtained from the curve-fitting, and plots of positon and FWHM of G peak as a function of pyrolysis temperature are shown in Figure 40(a) and Figure 40(b), respectively. It is seen, with increasing pyrolysis temperature, the position of G peak increases from 1585 cm\(^{-1}\) to 1606 cm\(^{-1}\) and the FWHM decreases from 112 to 52.
Figure 40: The peak position (a) and FWHM (b) of G peak as a function of pyrolysis temperature.

The activation energy for the free-carbon crystallization can be calculated according to the equation proposed by Ferrari et al.\textsuperscript{75}

\[ E = k T_c \ln(\nu \tau) \quad (7) \]

where \( k \) is Boltzmann constant, \( \nu \) is the phonon frequency of carbon which is \(~5\times10^{13}\), \( \tau \) is a constant about \(~1\) s, and \( T_c \) is a characteristic temperature where the structure of the amorphous carbon exhibits a sudden change. However, unlike previous reported polymer-derived SiC\textsuperscript{71} and SiCN\textsuperscript{73}, there is no sudden change in either peak position or FWHM.

As previously reported, the size of the free carbon clusters could be obtained by using the intensity ratio of the D-to-G peaks according to the Ferrar-Robertson equation.\textsuperscript{32, 76}

\[ \frac{I_D}{I_G} = C(\lambda) * L_a^2 \quad (8) \]
where \( C'(\lambda) = C_0 + \lambda C_1 \), \( C_0 = -12.6 \text{nm} \) and \( C_0 = 0.033 \), and \( \lambda \) is the wavelength of the excitation source (for \( \lambda = 514 \text{nm} \)). The carbon size as a function of pyrolysis temperature is plotted in Figure 41. The carbon size decreases with increasing pyrolysis temperature at first, then increases with increasing pyrolysis temperature, this phenomenon can be clearly interpreted by Ferrari Model\(^{32, 65}\) that the decrease in the size at first is due to the \( sp^3 \)-to-\( sp^2 \) transition and rearrangement of distorted aromatic rings to six-membered rings; and then the increase in the size at higher temperatures is due to the in-plane growth of nano-polycrystalline graphite. In addition, a sudden change point around 1100°C can be observed from Figure 41, assuming 1100°C is the characteristic temperature \( T_c \), the activation energy for the graphitization of free-carbon can be calculated as 3.73 eV, which is consistent with the reported value for crystallization of amorphous carbon\(^{75, 77, 78}\), but much smaller than that of the conduction change, suggesting the change in conductivity of the SiAlCO is not only dominated by the carbon crystallization.

\[ C'(\lambda) = C_0 + \lambda C_1, \quad (C_0 = -12.6 \text{nm} \text{ and } C_0 = 0.033), \quad \text{and } \lambda \text{ is the wavelength of the excitation source (for } \lambda = 514 \text{nm}). \]

The carbon size as a function of pyrolysis temperature is plotted in Figure 41. The carbon size decreases with increasing pyrolysis temperature at first, then increases with increasing pyrolysis temperature, this phenomenon can be clearly interpreted by Ferrari Model\(^{32, 65}\) that the decrease in the size at first is due to the \( sp^3 \)-to-\( sp^2 \) transition and rearrangement of distorted aromatic rings to six-membered rings; and then the increase in the size at higher temperatures is due to the in-plane growth of nano-polycrystalline graphite. In addition, a sudden change point around 1100°C can be observed from Figure 41, assuming 1100°C is the characteristic temperature \( T_c \), the activation energy for the graphitization of free-carbon can be calculated as 3.73 eV, which is consistent with the reported value for crystallization of amorphous carbon\(^{75, 77, 78}\), but much smaller than that of the conduction change, suggesting the change in conductivity of the SiAlCO is not only dominated by the carbon crystallization.

![Figure 41: Plot of the free carbon size as a function of pyrolysis temperature.](image)
X-ray photoelectron spectroscopy (XPS) are also used to further analyze the free-carbon phase within the material. According to the relative concentration of the four bonds estimated from the ratio of the integrated area under each peak listed in Table 7, the relative concentrations of C-Si and C-O bonds almost remain the same regardless of pyrolysis temperature. Additional, the relative concentration of C=C bond increases with the increasing pyrolysis temperature and the relative concentration of C-C/H bond decreases with the increasing pyrolysis temperature.

The $sp^3$-to-$sp^2$ transition can be described by the following reaction:

$$sp^3 \rightarrow sp^2$$

and the equilibrium equation of the reaction is

$$\frac{[sp^2]}{[sp^3]} = K = K_0 \exp \left( -\frac{\mu}{kT} \right)$$

where $[sp^3]$ and $[sp^2]$ are the concentrations for $sp^3$ and $sp^2$, respectively; K is the equilibrium constant, $K_0$ is a coefficient, k is the Boltzmann constant, and $\mu$ is the activation energy. Figure 42 is the plot of the natural logarithm of $[sp^2]/[sp^3]$ as a function of pyrolysis temperature [1000/T]. The activation energy of this reaction equals to 0.5635eV. This value is much smaller than the activation energy for $sp^3$-to-$sp^2$ transition of the free-carbon phase, which is 3.3-3.6eV$^{75,77,78}$. 

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Figure 42: Plot of the sp$^2$/sp$^3$ ratio as a function of pyrolysis temperature.

All the analytical results above suggest that the conduction mechanism of the increase in the conductivity with increasing pyrolysis temperature of the SiAlCO could be very complex. According to previous studies, if the change of conductivity of PDC attributes to the change of the conductivity of its free-carbon phase, the activation energy for the free-carbon graphitization and sp$^3$-to-sp$^2$ transition should be close to that of the conductivity change$^{71,79}$. For the SiAlCO, the activation energy for the conductivity change is not consistent with that for the graphitization of the free-carbon phase; meanwhile, the activation energy for sp$^3$-to-sp$^2$ transition of free-carbon is also much smaller than that for the conductivity change. These indicate the change of conductivity of SiAlCO is not only dominated by the structural change in the free-carbon phase.

Besides the effect of the structural evolution of the free-carbon phase, another factor that could affect the conductivity of the SiAlCO is the concentration of oxygen which forms C-O bond within the free carbon and/or form a layer between the matrix phase and the free-carbon phase. It
is well known that the conductivity of graphite strongly depends on oxygen concentration when oxygen acts as dopants within the graphite. On the other hand, the C-O layer between the matrix and free carbon phase can strongly isolate the electron transport from the matrix to the free carbon phase, increasing the overall resistivity. XPS spectra reveal that around 10% of C is bonded with O within the material. Although the relative concentration of C-O bond did not change with pyrolysis temperatures, the rearrangement of these bonds, such as from inside of the free carbon to the interlayer or reverse, with increasing pyrolysis temperature is highly possible. Thereby, we speculate that the change in the conductivity of the SiAlCO is possibly due to the redistribution of the oxygen within the material, which led to the increase in the conductivity of the free carbon phase.

4.4: Summary

The electric conduction behavior and microstructure of polymer-derived SiAlCO ceramics are studied. The conductivity of the material measured increased by ~ 6 orders of magnitude when the pyrolysis temperature increased from 1000\(^\circ\)C to 1400\(^\circ\)C, and the activation energy calculated from the Arrhenius relation between conductivity and pyrolysis temperature is 7.15eV, which is much higher than that of any reported PDC systems. The structure evolution of the free carbon phase is investigated by XRD, Raman spectroscopy and XPS. The results indicate that the change in the conductivity cannot be explained by the changes in the free carbon structure. We speculate that the conductivity change of the SiAlCO may because the redistribution of oxygen within the free carbon phase.
CHAPTER FIVE: COMPLEX IMPEDANCE SPECTRA

5.1: Introduction

Measuring electrical conductivity is an effective method to investigate the electrochemical properties of materials. Compared with dc-conductivity, which only provides simple quantitative measurement, ac-conductivity can provide more detailed information of materials. The impedance spectroscopy (IS) measures the dielectric properties of a medium as a function of frequency in an ac circuit. Impedance spectra measure the dielectric properties of a medium as a function of frequency. It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity. In fact, since the first use of IS to measure AC-conductivity of solid electrolytes in 1969, IS have been widely applied in the detection of ionic transport phenomena in various kinds of materials.

Previously, Chen introduced the concept of electric field concentration between free-carbon particles and concluded the pyrolysis-temperature induced increase in the conductivity of SiCN ceramic was mainly due to the conductivity increase of free-carbon phase. However, by analyzing the complex impedance spectra (IS) of SiCO ceramics, Wang reported the conductivities of both matrix and free-carbon phase increased as pyrolysis temperature increased. This phenomena indicates impedance spectroscopy can provide more detailed information about the change of conductivity of PDCs.

In this chapter, the complex impedance spectra of polymer-derived SiAlCO ceramics pyrolyzed at different temperatures are measured, and equivalent circuit models are used to analyze these spectra.
5.2: Experimental procedures

The SiAlCO ceramic samples are synthesized following the experimental procedures discussed in Chapter 3, and the complex impedance spectra of the samples are recorded for this study.

5.3: Results and discussion

Figure 43 shows the typical complex impedance spectra measured from the a-SiAlCO obtained at different temperatures in Nyquist plot. In order for comparison, the data were normalized with respect to the samples’ geometry according to following equation:

\[ \rho^*(\omega) = \rho'(\omega) - j \rho''(\omega) = Z^*/L \]

where \( L = (H/A) \), \( H \) is the thickness of the sample and \( A \) is the electrode area. It is seen that the samples prepared at 1000 and 1100°C show two semi-circles, while the sample prepared at 1200°C only shows one semi-circle, revealing the effect of pyrolysis temperature on the electric behavior of the material.
Figure 43: Nyquist plot of the complex impedance spectra of the SiAlCO synthesized at (a) 1000, (b) 1100 and (c) 1200°C. The black dots are experimental results, grey dash lines are the simulation results using the equivalent circuits shown in (d).

The spectra were further analyzed by equivalent circuit simulation. Previously, Wang et al.\textsuperscript{85} reported the complex impedance spectra of the bi-phased PDCs can be well-fitted by the equivalent circuit consisting of a series combination of two parallel Resistance-CPE circuits as shown in Figure 43(d), following a modified Debye model.\textsuperscript{86}

\[
Z^*(\omega) = Z'(\omega) - jZ''(\omega) = \sum_i \frac{R_i}{1 + Q_i R_i (j\omega)^s_i}
\]

(12)

where R is the resistance, Q is an empirical parameter, s is a constant in the 0~1 range, which can directly obtained from Z-View software. The equivalent true capacitance value \(C_i\) and relaxation time \(\tau\) then can be calculated according to Equation (13) and (14):

\[
C_i = Q_i \omega_s^{s_i - 1} = (Q_i R_i^{1-s_i})^{1/s_i}
\]

(13)
In this study, the impedance spectra were analyzed by using Z-View software. It is found that all three spectra can be well fitted by the equivalent circuit (Figure 43a, b and c), confirming that the samples have a bi-phased microstructure. The important fitting parameters are listed in Table 9. The parameters with subscript 1 are obtained from the first semi-circle (on the left-hand side of the spectra) and those with subscript 2 are obtained from the second semi-circle.

Table 9: Fitting parameters for SiAlCO ceramics.

<table>
<thead>
<tr>
<th>Pyrolysis Temperature (°C)</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance (R₁)</td>
<td>2.85E+06</td>
<td>1.66E+05</td>
<td>2.23E+04</td>
</tr>
<tr>
<td>Resistance (R₂)</td>
<td>2.50E+06</td>
<td>9.36E+04</td>
<td>5.67E+03</td>
</tr>
<tr>
<td>τ₁(s)</td>
<td>1.04E-05</td>
<td>4.80E-07</td>
<td>3.68E-07</td>
</tr>
<tr>
<td>τ₂(s)</td>
<td>4.98E-03</td>
<td>5.63E-05</td>
<td>3.30E-08</td>
</tr>
</tbody>
</table>

Data in Table 9 show that at each pyrolysis temperature, the resistances of the two phases are not much different from each other (the ratio of R₁ to R₂ is less than 4). Considering the samples only contain ~ 7 vol.% of the free-carbon phase, the resistivity of the free-carbon phase should be higher than that of the ceramic phase. This is different from the silicon carbonitride (SiCN) systems studied previously, where the free-carbon phase has much higher conductivity than the ceramic phase. This is likely due to the collective effect of followings: (1) the ceramic phase of the a-SiAlCO contains more than 56 vol.% of SiC which can have higher conductivity than amorphous carbon; and (2) the pyrolysis temperature is relatively low so that the free-carbon phase is still
highly disordered. The resistances of both phases decrease with increasing pyrolysis temperature, which is consistent with previous studies\cite{49, 73, 87}. Figure 44 plots the natural logarithm of R_1 and R_2 as a function of the reciprocal of pyrolysis temperature. It is seen that they all follow the Arrhenius relation. The activation energies calculated from the slopes for R_1 and R_2 are 3.87 and 4.86 eV, respectively. The activation energy for R_1 is similar to the typical activation energy for amorphous-to-nanocrystal transition of pure carbon, which was reported to be 3.3-3.6 eV\cite{77, 78}, suggesting that the first circle is likely associated with the free-carbon phase.

![Figure 44: Plot of the natural logarithm of resistivity of R1, R2 and R1+R2 (total resistance) as a function of pyrolysis temperature [1000/T].](image)

It can also been seen from Table 9 that C_1 increases slightly with pyrolysis temperature, but C_2 decreases significantly by more than 300 times when pyrolysis temperature increases from 1000 to 1200°C. In addition, C_1 is much smaller than C_2 for the sample pyrolyzed at 1000°C (C2-to-C1 ratio is more than 500 times); but the difference between the two decreases with increasing
pyrolysis temperature, and become similar for the sample pyrolyzed at 1200°C. The above behaviors can be rationalized by the structural evolution of the $\alpha$-SiAlCO with pyrolysis temperature. First, the change in the dielectric constant of the first circle is consistent with our assumption that the first circle corresponds to the free-carbon phase. The major structural change in the free-carbon phase is the increase in the degree of order$^{90}$; and usually dielectric constant is not sensitive to the degree of order for non-ferroelectric materials$^{91}$. Second, the significant decrease in the dielectric constant of the second semi-circle is likely due to the structural rearrangement in the ceramic phase. Previous studies revealed that with increasing pyrolysis temperature, the silicon tetrahedra, the major building blocks in the ceramic phase, undergo a transition from $\text{SiC}_2\text{O}_2$ to $\text{SiCO}_3$ and become more ordered. This change decreases the dipole density, thus reduces the dielectric constant.

Figure 45 plots the imaginary part ($Z''$) of the impedance spectra obtained from the samples pyrolyzed at different temperatures. The samples prepared at 1000 and 1100°C exhibit two relaxation peaks, while that prepared at 1200°C contains only one. Comparing the peak positions of these relaxations with the relaxation time in Table 9 reveals that for the samples obtained at 1000 and 1100°C, the relaxation peak at lower frequency is from the ceramic phase, and the one at higher frequency is from the free-carbon phase; while the relaxation peak in the sample pyrolyzed at 1200°C is from the free-carbon phase. One possible mechanism for relaxation is due to interface polarization, Maxwell-Wagner relaxation, which is usually observed in the systems consisting of two phases with significantly different resistances$^{93}$. It is obviously not the case in
our material since both phases in our material exhibit similar resistance. Thereby, the relaxations should be due to the phenomena occurred within each phase.

![Figure 45](image1.png)

**Figure 45: Plots of frequency-dependent imaginary part of the impedance for the samples pyrolyzed at (a) 1000, (b) 1100 and (c) 1200°C.**

To understand the relaxation processes, Figure 46 plots the frequency of the relaxation peaks as a function of pyrolysis temperature. It is found that these frequencies also follow Arrhenius relation. The activation energies calculated from the slopes are 3.4 and 6.1 eV for the free-carbon phase and the ceramic phase, respectively. For the free-carbon phase, the activation energy for the relaxation process is similar to that for the resistance, indicating that the changes in the resistance dominate the relaxation process in the free-carbon phase, which is consistent with that the capacitance of the free-carbon phase change slightly with pyrolysis temperature. Thereby, the increase in the relaxation frequency (or decrease in the relaxation time) in the free-carbon phase
is due to the increase in transport rate of the electrons. On the other hand, the activation energy for the relaxation in ceramic phase is about 1.3 eV larger than that for the resistance of the ceramic phase, indicating that the relaxation process is determined by both resistance and capacitance in the ceramic phase.

Figure 46: A plot of the relaxation frequency versus pyrolysis temperature for the relaxation from the free-carbon phase (circles) and the ceramic phase (squares).

5.4: Summary

In summary, the electric behavior of polymer-derived α-SiAlCO pyrolyzed at different temperatures is studied by impedance spectroscopy. The obtained spectra are analyzed by using equivalent circuit method. The results show that all the spectra can be well-fitted by a series combination of two parallel Resistance-CPE circuits, indicating that the material contains two phases, namely, the ceramic phase and the free-carbon phase. Unlike polymer-derived SiCN ceramics, the ceramic phase exhibits lower resistance than the free carbon phase in the α-SiAlCO.
Meanwhile the ceramic phase exhibits higher capacitance than the free-carbon phase. The resistance of both phases decreases with increasing pyrolysis temperature. While the capacitance of the free carbon phase only increases slightly with pyrolysis temperature; that of the ceramic phase drastically decreases. The results also reveal that the material contains two relaxation processes, one from each phase. With increasing pyrolysis temperature, the relaxation peak moves to higher frequencies. The change of the relaxation peak frequency for the free-carbon phase is mainly due to the change in resistance, while that for the ceramic phase is due to the changes in both resistance and capacitance. Above electric behaviors are discussed in terms of structural evolution in both phases.
CHAPTER SIX: STUDY ON THE TEMPERATURE-DEPENDENT CONDUCTIVITY AND ELECTRONIC STRUCTURE EVOLUTION OF POLYMER-DERIVED AMORPHOUS SiAlCO CERAMICS

6.1: Introduction

Among all the outstanding properties of PDCs, mechanical properties, thermal properties and electrical properties have been studied in detail, but their electronic structures only appealed little attentions. In fact, PDCs exhibit unique high-temperature semiconducting behavior\textsuperscript{94, 95} and they are potential materials for future high-temperature applications, therefore having a comprehensive understanding of their electronic structure is necessary. Combining temperature-dependent conductivity measurement and optical absorption measurement is an effective way to examine their electronic structures.

In this Chapter, the effect of the pyrolysis temperature on the electronic structure of SiAlCO ceramics is studied by measuring their temperature-dependent conductivity and optical absorption. The experimental results are analyzed via theoretical models and then the electronic structures can be demonstrated.

6.2: Experimental procedures

The synthesis procedures of samples have been illustrated in Chapter 3. DC-conductivity at high-temperature range and optical absorption spectra are used to analyze their electronic structures.
6.3: Results and discussion

Figure 37 plots the relationship between optical absorption coefficient ($\alpha$) and photon energy ($h\nu$) of the four samples pyrolyzed at different temperatures. Within the entire detecting photon energy range from 1.5 to 5eV, SiAlCO ceramics exhibit continuous absorption, which is a typical behavior of amorphous semiconductors.

Davis and Mott\textsuperscript{62} has demonstrated that at higher energy range, the absorbance and photon energy should follow the equation:

$$ (\alpha h\nu)^r \propto (h\nu - E_g) $$

(15)

where $E_g$ is the optical energy gap, $r$ is the exponent depending on the transition type in the K space\textsuperscript{62}. According to previous studies, for amorphous semiconductors, $r$ is equal to 2 when the transition happens between the two delocalized bands. The optical absorption spectra are replotted in form of $(\alpha h\nu)^2$ vs $h\nu$ in Figure 47, and the band gaps for the materials estimated by extrapolation are 3.588, 3.305, 3.235 and 2.881eV, respectively.
Figure 47: Plot of $(\alpha h\nu)^2$ as a function of photon energy, the band gaps for SiAlCO ceramics are estimated by extrapolation (dashed lines).

In addition, it can be seen from Figure 37 that the absorption coefficient does not equal to zero at lower photon energy range, indicating there should be other absorption mechanisms. Based on Andronenko’s studies\textsuperscript{96}, there should be a $T_{\text{auc}}$ absorption for amorphous semiconductors at lower photon energy range due to the transition from localized states to delocalized states, and follows equation:

$$\alpha h\nu = B(h\nu - E_T)^n$$

where $B$, $n$ are constants, $E_T$ is $T_{\text{auc}}$ band gap. According to Inkson\textsuperscript{97}, $n$ should equal to $\sim 1.5$ for a transition from a deep impurity trap to a delocalized band. Pfost\textsuperscript{98} also suggested when $n$ is around 1.5, there should be a relationship between $E_T$, $E_C$ and $E_D$, namely,

$$E_T = E_C - E_D$$
where $E_C$ is the edge of the extended conduction band and $E_D$ is a deep defect level with a high density of state. In order to inspect if the $T_{auc}$ transition from a deep impurity trap to a delocalized band exists in this material, the absorption behavior is measured in the low excitation energy from 0.5 to 0.75 eV. The experimental data is then analyzed using Equation (16) and plotted in Figure 48. It can be seen the experimental data can be well fitted by Equation (16) within the excitation range and the fitted value for constant $n$ is also around 1.5 (Table 10), which confirms the existence of $T_{auc}$ transition within the material.

![Figure 48: Plot of $\alpha h\nu$ as a function of the photon energy. The solid lines are experimental data; the open symbols are curve fits using Equation (16).](image-url)
Table 10: Fitting Parameters for the Optical Absorption Curves

<table>
<thead>
<tr>
<th>Pyrolysis temperature (°C)</th>
<th>$E_g$(eV)</th>
<th>$E_T$(eV)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>3.588</td>
<td>0.4</td>
<td>1.71</td>
</tr>
<tr>
<td>1100</td>
<td>3.305</td>
<td>0.3</td>
<td>1.71</td>
</tr>
<tr>
<td>1200</td>
<td>3.235</td>
<td>0.19</td>
<td>1.77</td>
</tr>
<tr>
<td>1300</td>
<td>2.881</td>
<td>0.18</td>
<td>1.51</td>
</tr>
</tbody>
</table>

For amorphous semiconductors, there are three conduction mechanisms: the conduction in extended states, the conduction in band tails and the conduction in localized states$^{99}$. Thus the temperature dependent conductivity of amorphous semiconductor can be described by Equation (18):

$$
\sigma = \sigma_1 e^{-\frac{E_C-E_F}{kT}} + \sigma_2 e^{-\frac{E_A-E_F+\omega}{kT}} + \sigma_3 e^{-\frac{T_0}{(T)}^{1/4}}
$$

where $E_C$, $E_A$ and $E_F$ are the mobility edge of conduction band, the band tail and the Fermi level, respectively. $\omega$ is the thermal activation energy, which equals to the phonon energy of the material (here we assume the phonon energy of SiAlCO is equal to that of graphite, which is 60 meV$^{100}$). $\sigma_1$, $\sigma_2$ and $\sigma_3$ are prefactors, which have no physical significance, and $T_0$ is a characteristic temperature. The first term is the contribution from the conduction in extended states, which occurs at the high-temperature range; the second term is the contribution from the conduction in band tail states, which occurs within the middle temperature range, and the third term is the contribution from the conduction in localized states, which occurs in the low-temperature range$^{101}$. The experimental data present in Figure 49 are analyzed by Equation (18) and all four samples can be
well-fitted, the excellent consistence indicates the conduction mechanism of SiAlCO can be described by amorphous semiconductor model. All fitting parameters are listed in Table 11.

![Figure 49: Plot of the electrical conductivity as a function of testing temperature. The open symbols are experimental data, and the solid lines are curve fits using Equation (7).](image)

**Table 11: Fitting Parameters for the Conductivity Curves**

<table>
<thead>
<tr>
<th>Pyrolysis Temperature (°C)</th>
<th>E_C-E_F</th>
<th>E_A-E_F+ω</th>
<th>T_0</th>
<th>σ_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>0.466</td>
<td>0.237</td>
<td>1.624E+7</td>
<td>6.046E-1</td>
</tr>
<tr>
<td>1200</td>
<td>0.322</td>
<td>0.165</td>
<td>6.714E+5</td>
<td>2.721E-3</td>
</tr>
<tr>
<td>1300</td>
<td>0.224</td>
<td>0.074</td>
<td>8.549E+4</td>
<td>4.654E-4</td>
</tr>
<tr>
<td>1400</td>
<td>0.213</td>
<td>0.070</td>
<td>8.818E+3</td>
<td>1.283E-4</td>
</tr>
</tbody>
</table>
Taking advantage of all parameters in Table 10 and Table 11, the electronic structures of the SiAlCO ceramics can be determined by the following principles:

- The conduction edge \( (E_C) \): \( E_C = E_g + E_v \), (assuming \( E_v = 0 \)).
- The band tail edge \( (E_A) \): \( E_A = E_C - (E_C - E_A) = E_C - [(E_C - E_F) - (E_A - E_F + \omega)] - \omega. \)
- Fermi energy \( (E_F) \): \( E_F = E_C - (E_C - E_F) \).
- Defect energy \( (E_D) \): \( E_D = E_C - E_T \).

The obtained electronic structures are schematically drawn in Figure 50. It can be seen the pyrolysis temperature have a significant effect on the electronic structures of SiAlCO.

Figure 50: A schematic of the electronic structures of the amorphous SiAlCO pyrolyzed at different temperatures.
6.3.1: Effect on the bandgap

Figure 51 plots the bandgap $E_g$ as a function of pyrolysis temperature and it is seen that $E_g$ decreases with the increasing pyrolysis temperature.

![Plot of the bandgap as a function of pyrolysis temperature.](image)

6.3.2: Effect on the band-tail

Figure 52 plots the change in the width of the band-tail ($E_C - E_A$) with increasing pyrolysis temperature. It is obvious that the band-tail width decreases with increasing temperature, and a sudden change point around 1100°C can be observed, which is consistence with previous research. It is known the existence of the band-tail is resulted from the deviation of an amorphous structure from periodic crystalline structure. The degree of order of the material can affect the band-tail width. Thus the decrease in the band-tail width suggests the increase in the degree of order of SiAlCO ceramics.
Figure 52: Plot of the band-tail width as a function of pyrolysis temperature.

6.3.3: Hopping mechanism

Previous studies showed that for amorphous semiconductor, if it follows the variable range hopping (VRH) mechanism, in which electrons transport within the defect energy level close to the Fermi level\textsuperscript{102, 103}, the prefactor $\sigma_3$ should have a relationship with $T_0$ as\textsuperscript{102}

$$\sigma_3 \propto (T_0^{-1/2})$$

(19)

if it follows the band-tail hopping (BTH) mechanism, in which electrons within the defect level fill empty states near a so-called “transport energy” and then hop back to lower localized states\textsuperscript{104, 105}, the prefactor $\sigma_3$ should have another relationship with $T_0$ which is\textsuperscript{104, 105}

$$\ln \sigma_3 \propto (T_0^{1/4})$$

(20)
Recently, polymer-derived SiOCN\textsuperscript{101} and SiC\textsuperscript{106} ceramics have been observed following the BTH mechanism. Thus, $\ln \sigma_3$ vs $(T_0^{1/4})$ is plotted in Figure 53, and it shows a very good liner dependence, which confirms the previous statement that PDCs follow the BTH mechanism.

![Figure 53: Plot of $\ln \sigma_3$ vs $(T_0^{1/4})$ for the four SiAlCO ceramic samples.](image)

According to the electronic structure of SiAlCO ceramics in Figure 50, it can be seen that the band-tail edge, defect energy level and Fermi level are close to each other, and the band-tails even extend into the defect energy level when pyrolysis temperature increases to 1200°C and above. This unique structure makes those defect electrons prefer to transport within these states rather than the defect energy level.

The overlapped electronic structures of PDCs may due to the unique synthesis route of PDCs. As known, polymer precursors are cross-linked at relative low temperature, at such “low” temperature they will have a very slow diffusion rate, making atom rearrangement become very
difficult. Two consequents will be resulted from the slow diffusion rate. Firstly, the defect due to the chemical bonds broken are hard to be removed, secondly, the network of the material will remain disordered, which finally result to the unique electronic structure.

6.4: Summary

In summary, the electronic structure of SiAlCO ceramics pyrolyzed at different temperatures are obtained by using combined measurements of temperature-dependent conductivity and optical absorption. Both the bandgap and band-tail width decrease with increasing pyrolysis temperature. And a sudden change point around 1100°C owing to the change of degree of order can be observed from the change of the band-tail width. The material also follows the BTH mechanism which is consistence with other reported PDCs, and the unique electronic structure is due to the large amounts of defects resulted from the low temperature cross-linking process of the polymer precursor.
7.1: Introduction

Piezoresistivity, where electric resistivity varies with external mechanical loading, is an interesting and useful behavior of materials. This phenomenon has been widely employed to make sensors for sensing pressure, acceleration, vibration, as well as chemical and bio species\textsuperscript{107}. In the past decades, persisting efforts have been devoted to searching for materials of higher piezoresistive coefficient for achieving sensors with better sensibility, higher accuracy, and wider sensing range. These previous efforts led to the discoveries of several material systems with very high piezoresistivity, including well-doped semiconductors, diamond films, and conducting-particle-reinforced-insulating-polymer composites\textsuperscript{108, 109, 110, 111}. However, these materials are not suitable for applications at high temperatures and harsh environments due to their structural and/or functional instability at elevated temperatures. On the other hand, high-temperature materials, such as SiC and Si\textsubscript{3}N\textsubscript{4}, typically exhibit low piezoresistive coefficient\textsuperscript{112, 113}. Due to the demanding for sensors for high-temperature systems, such as turbine engines, material processing and nuclear reactors, searching for high-temperature materials that have high piezoresistivity has received increasing attentions. PDCs are a perfect choice.

In this chapter, the piezoresistive behavior of SiAlCO ceramic is studied by using a uniaxial spring tester in a pressure range of 0 to 6.5MPa.
7.2: Experimental procedures

The synthesis and characterization procedures of samples follows Chapter 3. SiAlCO ceramics pyrolyzed at 1100°C are used for the piezoresistive test.

Disk samples of 10mm in diameter and 3mm in thickness are used to measure the piezoresistive behavior. Both sides of the specimens are painted with silver paste to form circular electrodes with diameter of 6mm. The specimens are then tested under uniaxial compressive stresses using Intercomp 100058 Valve Spring Tester (Intercomp Company, Medina, MN). The resistance is obtained by measuring their I-V curves on KEITHLEY 2400 (Keithley Instruments, Inc., Cleveland, OH). The Young’s modulus of the samples were measured by using Nanoindentation (HYSITRON, Inc., Minneapolis, MN) and the average value is 150GPa.

7.3: Results and discussion

Figure 54(a) plots the average resistance of several α-SiAlCO sample as a function of the applied stress at room temperature (25°C). It is seen that the resistance drastically decreases from ~90000 to ~55000Ω when the pressure increases from 0 to 7.5MPa, suggesting that the material should have a profound piezoresistive effect. The pressure-dependent resistance is measured during loading-unloading cycle repeatedly for four times (Figure 54(b)). The results show that the resistance of the sample is highly reproducible during the cycling test, indicating that the change in the resistivity is due to the elastic deformation rather than any plastic change in the material. Such a highly repeatable and elastic response is important from application point of view.
Figure 54: Plots of resistance as a function of the applied stress during increasing pressure (a) and for four loading-unloading cycles (b). The open circles are experimental data; and the solid line in (a) is the best curve fit using the displayed equation.
The piezoresistive effect of a material can be quantified by its piezoresistive coefficient (also known as gauge factor), \( K \), defined as

\[
K = \frac{dR}{R} \frac{d\varepsilon}{d\varepsilon} = E \frac{dR}{R} \frac{d\varepsilon}{d\sigma} = \frac{E}{\varepsilon} \frac{dR}{d\sigma} \tag{21}
\]

where \( R \) is the electric resistance, \( E \) is Young’s modulus of the materials (measured to be 150GPa for the \( a \)-SiAlCO), \( \varepsilon \) is the strain, and \( \sigma \) is the applied stress. In order to use Equation (21) to calculate the gauge factor, we first curve-fitted the experimental data shown in Figure 54(a) to obtain fitting equation. It is found that the resistance can be best fit by following equation:

\[
R = -56.8 \sigma^3 + 1097.1 \sigma^2 - 9812.2 \sigma + 90214 \tag{22}
\]

In this fitting equation, the unit of \( R \) is Ohm and the unit of \( \sigma \) is MPa. The gauge factor is then calculated using Equation (21) and (22) and plotted as a function of applied stress. It is seen that the \( a \)-SiAlCO exhibits an extremely high gauge factor in the range of \( \sim7000-16000 \), which is much higher than that of the PDCs reported previously and any existing high-temperature materials. This suggests that the SiAlCO is a very promising sensor material, which will lead to better sensitivity, higher accuracy and wider sensing range. The gauge factor decreases with increasing pressure, similar to those PDCs reported previously.
Further investigation of the piezoresistive behavior of the SiAlCO is carried out by measuring the resistivity of another SiAlCO sample prepared under same condition at different temperatures in range of 25-300°C. Figure 56(a) plots the resistivity of the SiAlCO as a function of temperature measured at two different pressures of 0 and 3MPa. It is seen that the resistivity of the sample decreases with increasing temperature at both pressures; and at a given temperature, the resistivity measured at 3MPa is always lower than that measured under no external applied pressure, indicating there is piezoresistive effect at all temperatures.
Figure 56: (a) Plot of the resistivity as a function of temperature measured at the stress of 0 and 3MPa, as labeled; (b) Plot of piezoresistive stress coefficient as a function of temperature.
To illustrate the effect of the temperature on the piezoresistive effect, the piezoresistive stress coefficient, \( \Pi \), of the material is calculated using following equation:

\[
\Pi = \frac{\Delta \rho / \rho}{\sigma}
\]  

(23)

where \( \rho \) is the resistivity of the material. Figure 56(b) plots the piezoresistive stress coefficient as a function of temperature. It is seen that the material exhibits a positive temperature-dependent piezoresistive stress coefficient – the coefficient increases with increasing temperature. This is fundamentally different from those reported previously for polycrystalline materials and PDCs, which all showed decrease in piezoresistive stress coefficient with increasing temperature.

The mechanism responsible for the positive temperature-dependent piezoresistive stress coefficient is not clear at this moment. There are two possible reasons. One of them is that the increase in temperature may lead to the decrease in Young’s modulus of the material, thus the same applied pressure induced more strain within the materials, especially in the graphene phase. The other mechanism could be that the increase in temperature affected the electron transport within the carbon phase. Previous study revealed that the transport of electrons within highly disordered carbon follows a hopping mechanism\textsuperscript{105, 114}. The applied pressure may induce the changes in state distribution and change the conductivity of the material.

7.4: Summary

In summary, we have studied the piezoresistive behavior of amorphous SiAlCO ceramic derived from aluminum tri-sec-butoxide modified silicone resin. We have demonstrated that the material exhibits an excellent reproducible piezoresistive effect with the gauge factor of 7000-
16000, which is much higher than that for any existing materials. We have also shown that the piezoresistive stress coefficient of the material increases with increasing temperature in the temperature range of 25-300°C, which is different from other materials reported previously. The unusual piezoresistivity of the $a$-SiAlCO is attributed to its unique structure where the self-assembled graphene-like free carbon phase and dominated the conductive behavior of the material. Thus, the piezoresistivity of the material is likely due to that of the graphene-like phase. The excellent piezoresistivity, together with that the silicone resin is low-cost and environmentally inert as compared to other polymeric precursors, makes the material become a very promising candidate for high-temperature sensor applications.
CHAPTER EIGHT: COUPLING EFFECT OF TEMPERATURE AND STRESS ON THE CONDUCTIVE BEHAVIOR OF AMORPHOUS SIALC

8.1: Introduction

One unique behavior of PDCs is that their conductivity strongly depends on temperature and stress, making them very promising for high-temperature sensing applications\textsuperscript{59, 115}. For example, PDCs exhibit well-behaved amorphous semiconducting behavior, which can extend to very high temperatures\textsuperscript{49, 94}. Meanwhile, it was reported that the piezoresistive gauge factor of a polymer derived amorphous silicon carbonitride (SiCN) can be as high as 4000, which is much higher than that for crystalline silicon carbide and silicon nitride, attributed to a tunneling-percolation effect\textsuperscript{53, 116}. Unlike crystalline materials, the high gauge factor of PDCs can be retained to very high temperatures\textsuperscript{117}. While the effects of temperature and pressure on the conductivity of PDCs have been well recognized, the detailed study on the coupling effect of pressure and temperature has not been explored yet.

In this chapter, the coupling effect of temperature and pressure on the conductivity of SiAlCO ceramic is studied in temperature range of 25 to 300\textdegree C under three different pressures of 0, 3 and 7.5MPa.

8.2: Experimental procedures

The synthesis and characterization procedures of samples follows Chapter 3. SiAlCO ceramics pyrolyzed at 1100\textdegree C are used for this piezoresistive test. Disk samples of 10mm in diameter and 3mm in thickness are loaded into a vertical tube furnace. The uniaxial pressure is
applied onto the samples. The electric conductivity is measured along the loading direction in a
temperature range of 25-300°C at different uniaxial pressures of 0, 3.0 and 7.5MPa.

8.3: Results and discussions

It is well known that the conductivity of a semiconductor as a function of temperature can be described by following equation\textsuperscript{118}:

\[ \sigma_{TP} = \sigma_0 p \exp\left[-\left(\frac{T_0 p}{T}\right)^{\frac{1}{\beta}}\right] \]  

(24)

where \(\sigma_{TP}\) is the conductivity at temperature \(T\) and pressure \(p\), \(\sigma_0 p\) and \(T_0 p\) are the prefactor and characteristic temperature for conductivity measured at pressure of \(p\), respectively, and \(\beta\) is a constant, depending on the conduction mechanism. For crystalline semiconductors, \(\beta\) should be equal to 1; while for three-dimensional amorphous semiconductors, \(\beta\) should be equal to 4. Figure 57 plots the electric conductivity as a function of temperature measured under the three pressures, in the format of Equation (24) by using \(\beta=1\) and \(4\), respectively. It is seen that the data measured at all three pressures agree well with Equation (24) when \(\beta=4\), indicating that the material exhibited well-defined amorphous semiconducting behavior within the testing temperature and pressure ranges studied here. This suggests that the applied pressure did not change the amorphous semiconducting nature of the materials. This is not something unexpected since the magnitude of the applied pressure is not sufficient to alter the amorphous nature of the material.
Figure 57: Plot the electric conductivity as a function of temperature measured under the three pressures, in the format of Equation (24) using $\beta=1$ and 4.

Table 12 lists the parameters determined by curve fitting the experimental data with Equation (24). It is very interesting to see that the characteristic temperature ($T_{op}$) increases with increasing pressure. Previous studies have demonstrated that the characteristic temperature of the 3-D amorphous semiconductors is related to the DOS within the energy level involved in the hopping process. Thereby, the results listed in Table 12 indicate that the DOS in the material was
altered by the applied external pressure. The effect of external pressure on the electronic structure has been widely studied for crystalline materials. For example, a uniaxial pressure can cause the decrease in the bandgap of n-type silicon along the loading direction and increase along other directions. However, the effect of the pressure on the electronic structure of polymer-derived amorphous materials has never been reported.

Table 12: Fitting parameters for Figure 57.

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>0</th>
<th>3</th>
<th>7.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{op}$</td>
<td>9.63E+7</td>
<td>1.43E+8</td>
<td>2.27E+8</td>
</tr>
<tr>
<td>$\sigma_{op}$</td>
<td>3.2E+5</td>
<td>4.7E+6</td>
<td>1.4E+8</td>
</tr>
</tbody>
</table>

To better understand the phenomenon, the detailed conduction mechanism of the material needs to be known. There are two hopping mechanisms that can lead to the $T^{1/4}$ dependence in amorphous semiconductors: variable range hopping (VRH) and band-tail hopping (BTH). They can be distinguished from each other by the relationship between the prefactor $\sigma_{op}$ and characteristic temperature $T_{op}$. That is for the variable range hopping process, the two parameters should vary in opposite directions; while for the band-tail hopping process, the two should vary in the same direction according to \(^{105, 119}\)

\[
\ln \sigma_{op} \propto T_{op}^{1/4}
\]  

(25)
Figure 58 plots $\sigma_{0P}$ as a function of $T_{0P}$ in the format of Equation (25). It is seen that the two follow the relation predicted by the equation very well, indicating the SiAlCO should exhibit the band tail hopping process, similar as other polymer-derived amorphous ceramics.

![Figure 58: Plot of $\sigma_{0P}$ as a function of $T_{0P}$.](image)

The BTH process is related to the exponential dependence of DOS within the band-tail level. Thereby, we believe that the change in the characteristic temperature is likely due to the change in the DOS in the band-tail of the material. Since the characteristic temperature is reversely related to the DOS, the DOS in the band-tail should decrease with increasing applied pressure. This can be understood as follows. The presence of the band-tail level in amorphous semiconductors is due to their disorder structure as compared with ordered structure in crystal materials. The applied pressure can cause the decrease in the specific volume ($\Delta v = V_o \left(1 - \frac{P}{E} (1 - 2\nu)\right)$, where $V_o$ is the original specific volume, $E$ is the Young’s modulus and $\nu$ is the
Poisson’s ratio of the material). Such a decrease in the specific volume can lead to certain degree of ordering (higher packing density of the atoms) within the material to reduce the density of states within the band-tail.

Figure 57 also reveals that at any given temperature the conductivity of the material increases with increasing pressure, suggesting that the material exhibits negative piezoresistivity (resistivity decreases with increasing stress). The piezoresistivity of a material can be quantitatively described by its piezoresistive stress coefficient, $\Pi$, defined as,

$$\Pi = \frac{(\rho_{T0} - \rho_{Tp})/\rho_{T0}}{p} = \frac{1 - \sigma_{Tp}/\sigma_{T0}}{p}$$  \quad (26)$$

where $\rho_{T0} (= 1/\sigma_{T0})$ and $\rho_{Tp} (= 1/\sigma_{Tp})$ are the resistivity measured at temperature $T$ and pressures of 0 and $p$, respectively. By taking the data from Figure 57, the coefficient was calculated at different temperatures and plotted in Figure 59(a). It is seen that at any temperature, the piezoresistive stress coefficient obtained at 7.5MPa is lower than that obtained at 3MPa; which is consistent with our previous results which showed that the piezoresistive stress coefficient of polymer-derived amorphous materials decreased with increasing the pressure. The figure also reveals that at a given pressure, the coefficient increases with increasing temperature. This last phenomenon is very interesting since it is contradictory to previous studies, which showed that the piezoresistive stress coefficient decreased with increasing temperature.
Figure 59: Plots of (a) piezoresistive stress coefficient and (b) modified piezoresistive stress coefficient as a function of temperature, measured at different pressures as labeled.

As discussed above, the conductivity of the material changed with both temperature and pressure. Such coupling effect is also reflected by that the pressure can change the characteristic temperature of the material. It is seen from Table 12 that $T_{op}$ increases with elevated pressure.
According to Equation (24), the temperature has more effect on the conductivity at higher pressures. This could be the reason why the material exhibited the increased piezoresistive stress coefficient with the pressure. To quantitatively demonstrate this, we modified the conductivity measured at the different applied pressures/temperatures by using the following equation, to remove the effect of the characteristic temperature:

$$\sigma'_{TP} = \frac{\sigma_{TP} \exp\left[-\left(\frac{T_0}{T}\right)^{\frac{1}{4}}\right]}{\exp\left[-\left(\frac{T_0P}{T}\right)^{\frac{1}{4}}\right]}$$

(27)

The modified piezoresistive stress coefficient can then be calculated by

$$\Pi' = \frac{1 - \sigma_{T0}/\sigma'_{TP}}{p} = \frac{1 - \sigma_{T0} \exp\left(-\frac{1}{T_0P - T_0}\right)}{p \frac{1}{T^4}}$$

(28)

Figure 59(b) plots the modified piezoresistive stress coefficient as a function of temperature. It is seen that the modified coefficient is independent of temperature. The result clearly demonstrates that the increase in the piezoresistive stress coefficient with temperature is due to the effect of the pressure on the characteristic temperature of the material. The fact that the modified coefficient is independent of temperature suggests that the Young’s modulus of the material remains the same with increasing temperature within the temperature range tested here, which is reasonable due to the covalent bond nature of the material.

8.4: Summary
In summary, the coupling effect of temperature and stress on the piezoresistive behavior of SiAlCO ceramic has been studied here. Within the temperature and pressure ranges tested here, the material exhibits amorphous semiconducting behavior and its conductivity increases with increasing both temperature and pressure. By comparing the experimental data with theoretical model, we find that the characteristic temperature for BTH increases with increasing pressure, suggesting that the band-tail structure is changed by the applied pressure. The piezoresistive stress coefficient of the material increases with increasing temperature, which is different from all results reported previously. It is found that such increase in the piezoresistive stress coefficient is due to the change in the characteristic temperature.
CHAPTER NINE: ANOMALOUS PIEZO-DIELECTRICITY OF POLYMER-DERIVED AMORPHOUS SIALCO

9.1: Introduction

Silicon-based amorphous materials prepared by pyrolyzing polymeric precursors (named polymer-derived ceramics, PDCs) have received extensive attentions in the past years, not only because of their promising for many practical applications but also because of their unique structure and properties. PDCs possess a bi-phased structure consisting of the amorphous ceramic phase and highly-disordered free-carbon phase which mangle together to split each other into domains of nanometer-size. Due to the highly non-equilibrium nature of the pyrolysis process, PDCs contain a large amount of defects such as dangling bonds and mixing bonds. This structure confers many unusual properties to the materials, including tunable conductivity, high-temperature semiconducting behavior, and piezo-resistivity.

In this chapter, we study on the piezo-dielectricity of polymer-derived amorphous silicoaluminum oxycarbide (a-SiAlCO). Piezo-dielectricity, where the dielectric constant varies with applied stress, has been a persisting subject of material science and solid-state physics because it is related to many fundamental physics of a material, such as lattice structure, defect/impurity states, and optical/transport properties. Recently, the interests on this topic is renewed due to its potentials for dielectric sensors. We reveal that the a-SiAlCO exhibits anomalous piezo-dielectricity with the pressure coefficient of the dielectric constant much higher than that of other existing materials. It is demonstrated that the increase in the dielectric constant is mainly due to the increase in the polarizability, resulting from the unique structure of the material.
9.2: Experimental procedures

The synthesis and characterization procedures of samples follows Chapter 3. The dielectric constant of the a-SiAlCO is measured at different uniaxial pressures. First, the surfaces of the obtained disk-shaped samples are ground and polished to ~1 µm finish. The process is carried out carefully to keep the two surfaces of each sample parallel to each other. The indium–gallium paste is then painted on the surfaces of the samples as the electrodes. A uniaxial pressure is applied onto the sample by the Intercomp 100058 Valve Spring Tester (Intercomp Company, Medina, MN). The dielectric constant of the sample is recorded at the frequency of 100 kHz at room temperature using an impedance analyzer (Agilent4294A; Agilent Technologies, Santa Clara) with an accessory (16034G). The measurement is carried out at various pressures up to 1.2 MPa during both loading and unloading.

9.3: Results and discussions

Figure 60 shows the dielectric constant as a function of the applied pressure for 4 loading-unloading cycles. While the data obtained from different testing runs are not fully repeatable, the maximum deviation between the data measured at the same pressure is less than 5%, suggesting that the observed piezo-dielectric behavior is highly reliable. The results reveal that the dielectric constant of the a-SiAlCO is ~ 350 without pressure, which is very high compared to most of materials. The dielectric constant increases with increasing pressure, indicating that the material exhibits a positive pressure coefficient of dielectric constant. The high reproducibility, together with the fact that the data obtained at the same pressure does not increase (or decrease) monolithically with the sequence of testing runs, suggest that the change in the dielectric constant with pressure is due to elastic deformation.
Figure 60: A plot of dielectric constant as a function of the applied pressure for four loading/unloading cycles. The filled symbols are measured during loading, and the open symbols are measured during unloading.

The rather high dielectric constant of the \(a\)-SiAlCO is quite unique. The value is much higher than that of the materials without spontaneous polarization, and comparable to that of ferroelectric materials\(^{129}\), materials with boundary-layer-capacitance (BLC) effect\(^{131}\), and dielectric polymer composites consisting of insulating matrix and dispersed conducting particlres\(^{130}\). The polarization mechanism for BLC materials and dielectric polymer composites is similar and is the space charge at the interfaces between conducting particles (grains) and insulating matrix (grain boundary). While the \(a\)-SiAICN also contains two phases, these two phases exhibit similar conductivity, thus space charge cannot be the polarization mechanism for the material. We believe that the high dielectric constant of the \(a\)-SiAlCO is due to the existence of a long amount of self-formed dipoles in the material. It is well unknown that PDCs possess a large amount of point defects (e.g. C-dangling bonds); and the \(a\)-SiAlCO also contains mix-bonded silicon tetrahedra, SiCO\(_3\) and
SiC$_2$O$_2.$ The dipoles likely come from these dangling-bonds and mix-bonded silicon tetrahedra, which result in unsymmetrical distribution of electrons. For example, within the SiCO$_3$ tetrahedra, the negative charge are more toward the oxygen ions, leading to dipoles within the tetrahedra.

Piezo-dielectricity of a material can be quantitatively described by its pressure coefficient of the dielectric constant, defined as:

$$K = \frac{d\epsilon/\epsilon}{dp} = \frac{\partial \ln \epsilon}{\partial p}$$

(29)

where $\epsilon$ is the dielectric constant and $p$ the applied pressure. Figure 61(a) plots the logarithm of dielectric constant versus the applied pressure, using the average value of the data obtained from the eight runs. The tangent slope of such a plot is the pressure coefficient of the dielectric constant at a given pressure. Figure 61(b) shows the pressure coefficient of the dielectric constant of the a-SiAlCO as a function of the pressure. The coefficient decreases from 0.25 and 0.10 MPa$^{-1}$ with the pressure increasing from 0.1 to 1.2 MPa. It is interesting to note that these values are much higher than that of previously reported materials without spontaneous polarization$^{125, 126},$ and even more than two times higher than that of ferroelectric strontium titanate$^{128}.$
Figure 61: Plots of logarithmic dielectric constant (a) and pressure coefficient of the dielectric constant (b) versus the applied pressure.

The dielectric constant of a material can be related to its polarizability by the well-known Clausius-Mossotti (CM) relationship\textsuperscript{132, 133},

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi \alpha}{3V}
\]  

(30)

where \(\alpha\) is the polarizability of the material of volume \(V\). By differentiating the equation with respect to pressure, Gibbs and Hill obtained\textsuperscript{134}

\[
k = \frac{\partial \ln \varepsilon}{\partial p} = \frac{(\varepsilon - 1)(\varepsilon + 2)}{3\varepsilon} \left( \frac{\partial \ln \alpha}{\partial p} + \beta \right)
\]  

(31)

where \(\beta = -\partial \ln V / \partial p\) is the compressibility of the material. Equation (31) suggests that the pressure-induced dielectric-constant change is due to the changes in both volume and polarizability of the material.
The compressibility of the a-SiAlCO can be estimated from its elastic properties using the following equation:

$$\beta = \frac{\partial V/V}{\partial p} = \frac{3(1-2v)}{E}$$  \hspace{1cm} (32)

where $E$ and $v$ are the elastic modulus and Poisson’s ratio of the material, respectively. Elastic modulus of the a-SiAlCO was measured under uniaxial compressive testing to be 150GPa. By assuming Poisson’s ratio of the material to be 0.1-0.3, the $\beta$ for the a-SiAlCO is estimated to be 0.8-1.6x10^{-5} \text{MPa}^{-1}. Comparing the $k$ values in Figure 61(b) and the $\varepsilon$ values in Figure 60 indicates that the volume-change contribution to the pressure coefficient of the dielectric constant is very small and can be neglected. Thereby, the increase in the dielectric constant of the a-SiAlCO with pressure is mainly due to the increase in the polarizability of the material. Thereby, the change in the polarizability of a material with the applied pressure can be obtained by rearranging Equation (31),

$$\frac{\partial \ln \alpha}{\partial p} = \frac{3 \partial \ln \varepsilon}{\varepsilon \partial p}$$  \hspace{1cm} (33)

This can be defined as the pressure coefficient of the polarizability of the material. Figure 62 plots the pressure coefficient of the polarizability as a function of the applied pressure for the a-SiAlCO. It is seen that the coefficient is positive, indicating that the polarizability increases with increasing pressure. The coefficient decreases with increasing the pressure, indicating that the change in the polarizability becomes harder with increasing pressure.
Figure 62: A plot of pressure coefficient of the polarizability versus the applied pressure.

It is very interesting that the $a$-SiAlCO exhibits very high positive pressure coefficient of the dielectric constant and its polarizability increases significantly with the applied pressure. As we discussed above, the polarization mechanism of the $a$-SiAlCO is not space-charging but “spontaneous” polarization, similar to ferroelectric materials. However, the pressure coefficients of the dielectric constant for ferroelectric materials is large but negative since the applied pressure caused the decrease in spontaneous polarization by decreasing the distance between the positive charge center and negative charge center. The different behavior between conventional ferroelectric materials and the $a$-SiAlCO is likely due to the unique structure of the later. It is well unknown that PDCs possess a rather open structure with high free volume (the density of PDCs is much lower than that of their crystalline counterparts with the same composition). The free volume is not unevenly distributed, rather forms a cell-like structure with many large cavities. When the pressure is applied, such cavities will become “flatter” to reduce the overall volume. While the overall stress applied on the material is compressive, the stress on some parts of the wall of the
cell can be tensile. These parts will get elongated, and the distance of the dipole in the area increase, leading to the increase in dipole moments, thus the polarizability and dielectric constant. Deformability of the cavities will be decreased within increasing deformation, leading to the decrease in the pressure coefficient with pressure (Figure 62). This model is consistence with the previous result on the electronic structure of the material, where it was found that the density of the state (DOS) within the band-tail of the $a$-SiAlCO decrease with increasing pressure$^{136}$.

9.4: Summary

In summary, the room-temperature dielectric constant of the polymer-derived $a$-SiAlCO is measured at different pressures. The material exhibits a fairly high dielectric constant, which is within the range of those for ferroelectric materials, BLC materials and dielectric polymer composites. By comparing the polarization models and the unique structural features of the $a$-SiAlCO, we propose that the high dielectric constant of the material is due to the spontaneous polymerization associated with its point defects and mixing bonds. The $a$-SiAlCO also exhibits an anomalous piezo-dielectric behavior with a large positive pressure coefficient of the dielectric constant; and its polarizability also increases significantly with increasing pressure. This seems contradictory to the spontaneous polarization mechanism, which generally leads to a negative pressure coefficient of the dielectric constant and decrease in polarization with pressure. We attribute such contradiction to a unique cell-like structure of the polymer-derived $a$-SiAlCO. The large pressure coefficient of the dielectric constant is very promising for making dielectric sensors.
CHAPTER TEN: PRESSURE SENSOR DEVELOPMENT USING POLYMER-DERIVED SIALCO CERAMIC

10.1: Introduction

Sensors for pressure measurement in high temperature environment, such as power generation, aeronautical propulsion and nuclear reactors, are highly desirable for improving the performance and safety of the system\textsuperscript{137, 138, 139}. However, developing such sensors is very difficult. The biggest challenge is that the sensing materials must be able to structurally and functionally survive in the extreme environments including high temperatures, high pressure, corrosive species, and sometime radiations. In such environments, traditional silicon based transducers can no longer be used\textsuperscript{140}. New materials that have abilities to withstand high temperatures and provide reliable measurements need to be developed.

PDCs are preferred option due to their excellent thermal stability and high gauge factors even in high-temperature environments\textsuperscript{53, 141}. Several PDC-based temperature sensors have been developed, however the success of using PDCs to make pressure sensors has not been reported yet. Thus, in this chapter, a pressure sensor made of a SiAlCO ceramic is fabricated, characterized and tested, the results indicate this PDC-based pressure sensor is stable and reliable with a high sensitivity.

10.2: Fabrication and characterization of the ceramic sensor head

The sensor head is made of the polymer-derived SiAlCO ceramic with anomalous piezoresistive effect. The synthesis of the SiAlCO ceramic has been illustrated in Chapter 3, and
the obtained SiAlCO ceramic is shaped as disks of ~ 9.5mm in diameter and 3.0mm in thickness. The silver paste is placed on both side of the disk to form the sensor heads.

To know the characteristics of the sensor head, its resistance change as a function of applied pressure is studied under room temperature. Figure 63 shows the resistance of the sensor head as the pressure increases from 0 to 6.05MPa with an increment of 0.605MPa. It is seen that the resistance of the sensor head decreases with pressure monotonically, confirming that it is suitable for pressure sensing. The resistance of the sensor head is within a range of 13.5~15.5kΩ, which is in a good range for resistor-based sensors.

![Figure 63: Resistance of the PDC sensor head as a function of the applied pressure.](image)

The sensitivity of the sensor head can be evaluated by its piezoresistive coefficient,

\[ K = \frac{E(dR/R)}{dP} \]  \hspace{1cm} (34)
where $R$ is the electric resistance, $P$ is the applied pressure, and $E$ is Young’s modulus of the materials (measured to be 150GPa for the a-Si(Al)CO). By using the data in Figure 63, the coefficient of the sensor head is calculated to be $3000\text{~}5000\text{MPa}^{-1}$, indicating that the sensor head can be very sensitive.

In the above characterization process, the resistance of the sensor head is measured under known pressures. The pressure measurement process is a reversed process of finding pressure while knowing the resistance of the sensor head. Here, the resistance-pressure relationship of the sensor head can be modeled using the following empirical third order polynomial function:

$$P = \sum_{i=0}^{3} \alpha_i R^i \quad (35)$$

where $\alpha_i$ are constant coefficients, as shown in Table 13. These coefficients are obtained by curve-fitting the data in Figure 63. Figure 64 compares the actual and curve-fitting data results which are calculated by Equation (35). It can be seen that the curve-fitting pressure data matches well with those are applied on the testing bed. The excellent agreement between them suggests that the pressure-dependent resistance of the sensor head can be represented by Equation (35).
Figure 64: Pressure-resistance relationship; comparison of the actual and curve-fitting result.

Table 13: The constants used in Equation (35).

<table>
<thead>
<tr>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.6369</td>
<td>28.52</td>
<td>-427.8</td>
<td>2152</td>
</tr>
</tbody>
</table>
10.3: Sensor design

To make the material an independent sensor, additional supportive circuit is needed. As shown in Figure 65, the supportive circuit is consist of a divider resistor $R_o$ and the sensor head $R_p$. The resistance change of the sensor head will be reflected in the voltage change over the divider resistor. The relationship between the output $V_o$ and the resistance of the sensor head $R_p$ is given by:

$$V_o = \frac{V_s}{R_o + R_p} R_o$$  \hspace{1cm} (36)

where $V_s$ is the constant voltage of the power source. Then, the range of the output voltage can be expressed as:

$$V_r = V_{o,max} - V_{o,min} = \left(\frac{V_s}{R_o + R_{p,min}} - \frac{V_s}{R_o + R_{p,max}}\right) R_o$$  \hspace{1cm} (37)

where $V_{o,max}$ and $V_{o,min}$ are the voltages of the divider resistor when the sensor head was loaded with the maximum and minimum pressures, respectively; $R_{p,max}$ and $R_{p,min}$ are the resistance of the sensor head when it is loaded at maximum and minimum pressure, respectively.

![Circuit of the designed sensor.](image)

Figure 65: Circuit of the designed sensor.
To increase the accuracy of the sensor, the sensitivity of the sensor can be optimized by selecting a proper divider resistor. The optimal resistance of the divider resistor satisfies:

$$\frac{\partial V_r}{\partial R_o} = 0$$  \hspace{1cm} (38)

Solving Equation (38), it is obtained that the best sensitivity can be achieved for the sensor by choosing the resistance of the divider resistor,

$$R_o = \frac{R_{p,\text{min}}\sqrt{R_{p,\text{max}}} - R_{p,\text{max}}\sqrt{R_{p,\text{min}}}}{\sqrt{R_{p,\text{min}}} - \sqrt{R_{p,\text{max}}}}$$  \hspace{1cm} (39)

10.4: Experiment setup and results

In this paper, the sensor is tested under the room temperature and the change of pressure is in the range of 0Mpa to 6.05Mpa. According to the resistance of PDC sensor (i.e. as shown in Figure 63) and Equation (39), $R_o$ is chosen as 14.6KΩ.

Figure 66 shows the experimental setup of the pressure sensing system. The computer and the sensing system are interconnected by a data acquisition (DAQ) system (National Instrument, Austin, TX), which includes a real-time controller (PXI-8108), an analog input/output DAQ card (PXI-6221), and a signal terminal box for flying leads connection (SCB-68 conditioning block). The sensor head was placed on a pressure testing bed, and connected with an electrical circuit. The change in the resistance of sensor head due to pressure is reflected by the change of voltage of the divider resistor, which can be measured by PXI-6221. PXI-6221 is also used to provide external power supply to the electrical circuit. The sensor is tested for 6 cycles. In each cycle, the force (pressure) is first increased from 0kg (0Mpa) to 50kg (6.05Mpa), with an increment of 5kg
(0.605Mpa) each time. Then the force (pressure) is decreased from 55kg (6.05Mpa) to 0kg (=0Mpa), with a decrement of 5kg (0.65Mpa) each time.

![Diagram of sensor testing platform]

**Figure 66: Schematic diagram showing the sensor testing platform.**

10.4.1: Analysis of feasibility, stability, and repeatability

Figure 67 shows the output voltage (i.e. the voltage of the divider resister) as a function of pressure measured using the set up shown in Figure 66. It can be seen that the output voltage monotonously increases with increasing pressure.

Figure 68 shows the voltage output in one experimental cycle. The solid line shows the real-time change of the output voltage, and the imaginary lines show the force added on the sensor. Due to the limitation of the force testbed and the disturbance caused by manual operations, there are some noticeable variance in the form of noise, such as the impulse at sample time 1500. The overall trends show that: 1) the output voltage remains constant unless the force added on the sensor head is changed (e.g. The output voltage is about 4.9V when the added force is 0kg, and it changes to 4.94V when the added force is 5kg.); and 2) the output voltage under the same pressure during the pressure increasing and decreasing process are the same (e.g. The output voltages are
all around 4.9V when the force are increased to 5kg and decreased to 5kg). Thus, the PDC pressure sensing system is stable.

**Figure 67:** Relationship between the voltage of shunt resistor and the pressure.

**Figure 68:** Voltage output in one experimental cycle.
Figure 69 shows the output voltage as a function of pressure in all 6 cycles. Different colors represent different cycles. It is worth noting that each cycle has both pressure increasing and decreasing processes. It is clear that in each cycle the sensor produced almost identical responses under the same pressure during the compression and decompression process. Also, the sensor can produce almost identical responses in all of the 6 cycles and shows a very good repeatable performance.

Figure 69: Voltage output in six experimental cycles.

10.4.2: PDC sensor for actual pressure measurements

For pressure measurement purpose, the voltage output needs to be converted to pressure by using Equation (40), which can be derived by combining Equation (35) and (36).

\[
P = \sum_{i=0}^{3} a_i \left( \frac{V_i}{V_o} R_o - R_o \right)^i
\]  

(40)
To eliminate the error from manual operations and tester, the average output values from Figure 69 is used to calculate the pressure. The results are then compared with the load indicator on the tester (INTERCOMP 100058) and are shown in Figure 70. The high agreement of calculated pressure and the applied pressure to the sensor shows that the sensor can measure the pressure accurately.

Figure 70: Comparison of data measured by the pressure testing bed and designed pressure sensor.

10.5: Summary

In this chapter, a pressure sensor that has potential to use in the high temperature applications is designed and tested. The sensor head is fabricated by using polymer-derived SiAlCO ceramics. These PDC material can be used for high temperature applications due to its high temperature resistance and high gauge factor. Then the sensor head is connected with a divider resistor. The sensor is tested on a commercial force testing bed under room temperature. For pressure measurement, the output voltage of the divider resister is first measured by a DAQ device,
and then is converted to the pressure by mathematical derivation. The accuracy, stability, and repeatability of the sensor are validated through the experiments. Since the previous research shows that the resistance of the PDC material can monotonically decrease with increasing pressure and has high stability even in the high temperature environment, this pressure sensor can also be used in the high-temperature applications.
CHAPTER ELEVEN: CONCLUSIONS

In summary, the SiAlCO ceramics synthesized by using polysiloxane as polymer precursor, aluminum tri-sec-butoxide as al-modifier and ethanol as solvent are successfully obtained via polymer-to-ceramic route. All SiAlCO samples are amorphous ceramics with a chemical composition of SiC\textsubscript{0.93}O\textsubscript{0.57}Al\textsubscript{0.03}, and all samples almost remain the same regardless of pyrolysis temperature. By using XRD, Raman spectroscopy, XPS, impedance spectroscopy, optical absorption and piezoresistive behavior testing, several conclusions can be made.

Firstly, the conductivity of SiAlCO ceramic increases by ~6 orders of magnitude when the pyrolysis temperature increases from 1000\textdegree{}C to 1400\textdegree{}C, and the activation energy calculated from the Arrhenius relation between conductivity and pyrolysis temperature is 7.15eV, which is much higher than that of any reported PDC systems. The change in the conductivity of the SiAlCO ceramics may due to the redistribution of oxygen within the free-carbon phase.

Secondly, the complex impedance spectra of polymer-derived SiAlCO ceramics pyrolyzed at 1000, 1100 and 1200\textdegree{}C are measured and analyzed by using equivalent circuits. It is found that all the spectra can be well-fitted by a series combination of two parallel Resistance-CPE circuits, indicating there should be two impedance mechanism, namely, via the matrix and free-carbon phase. The resistivity of both phases decreases with increasing pyrolysis temperature, owing to the increase of ordering degree in both phases. The relaxation time obtained from the equivalent circuit simulation suggests that the ordering process almost finished at temperature of 1100\textdegree{}C, while the structural evolution for the matrix phase continued to 1200\textdegree{}C.
Thirdly, the electronic structure of the SiAlCO ceramics are obtained via combination measurements of temperature-dependent conductivity and optical absorption. The results suggest the conduction mechanism of this material can be described by amorphous semiconductor model. In addition, it follows the BTH process because of the unique electronic structure resulted from the low-temperature crosslinking process.

Fourthly, the piezoresistive behavior of amorphous SiAlCO ceramic is also investigated. The material exhibits an excellent reproducible piezoresistive effect with the gauge factor of 7000-16000, which is much higher than that for any reported high-temperature materials. The piezoresistive stress coefficient of the material increases with increasing temperature in the temperature range of 25-300°C, which is contradictive to other materials reported previously.

Fifthly, the coupling effect of temperature and pressure is studied. Within the testing temperature and pressure ranges, the material exhibits amorphous semiconducting behavior and its conductivity increases with increasing both temperature and pressure. The characteristic temperature for BTH process increases with increasing pressure, suggesting that the density-of-state within band-tail level is changed by the applied pressure. The piezoresistive stress coefficient of the material increases with increasing temperature, which is due to the change in the characteristic temperature.

Sixthly, the material exhibits a fairly high dielectric constant within the range of those for ferroelectric materials, BLC materials and dielectric polymer composites, which is due to the spontaneous polymerization associated with its point defects and mixing bonds. The a-SiAlCO
also exhibits an anomalous piezo-dielectric behavior with a large positive pressure coefficient of the dielectric constant; and its polarizability also increases significantly with increasing pressure.

In the end, a PDC-based pressure sensor used in high temperature environment is fabricated successfully. The sensor head is connected with a divider resistor and tested via a compression spring tester. The output voltage of the divider resistor is first measured by a DAQ device, and then is converted to the pressure by mathematical derivation. The accuracy, stability, and repeatability of the sensor are validated through the experiments.
REFERENCE


