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Junhang Dong, PhD
Development of Copper-Doped Zirconia Incorporated Fiber Optic Sensors for High Temperature Carbon Monoxide Detection

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By

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Abstract

Fiber optic chemical sensors made by integrating thin films of chemically sensitive inorganic materials and structured fiber have shown great promise for in situ chemical detection in various harsh conditions where traditional electrochemical sensors are inefficient to operate. The goal of this thesis research is to develop new long period fiber grating (LPFG) based fiber optic sensors (FOS) utilizing nano structured copper-doped-zirconia (CDZ) thin films as CO sensing material for applications in high temperature environments. The sensor operates by measuring the LPFG resonant wavelength ($\Delta\lambda_R$) shift caused by the variation of CDZ film refractive index upon contacting CO-containing gases. The fundamental cause of the CDZ refractive index change in different atmospheres is the reversible Red-Ox reactions of the CuO dopant, i.e. $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ in CO-containing reducing atmosphere and $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$ in oxidizing gases. These redox reactions result in variations of defect types and populations, electron states, electrical conductivity, material density, lattice parameters, and consequently optical properties of the CDZ oxide thin film.

This thesis research includes three parts: (1) identification and optimization of conditions for coating the CDZ thin film on the LPFG, (2) demonstration of the CDZ-coated LPFG (CDZ-LPFG) for high temperature CO sensing, and (3) investigation on the relationship between the CO sensing performance and the CDZ material composition. The results of this research indicate that the CDZ nanocrystalline thin film coated LPFG sensors can be used for detection of low concentration CO at temperature of $>500^\circ$C. It has been also found that over reduction of the Cu$^{2+}$ dopant to Cu$^0$ (metal) occurs in gases containing high-concentration CO to cause CDZ material instability and hence sensor irreversibility. The Cu$^{2+}$ to Cu$^0$ over reduction caused sensor instability is irreversible because of the segregation of Cu$^0$ from the CDZ crystal phase to the grain boundaries. Therefore, the CDZ-LPFG sensors are potentially useful as safety sensors or for post-combustion gas monitoring at high temperature but not suitable for bulk CO composition measurement.
Acknowledgement

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I would also like to thank my committee members for giving me suggestions to help guide my research and the way my research was completed. I would especially like to thank Dr. Junhang Dong for serving as my advisor. Through all the troubles and problems that go along with research he maintained patience and confidence that I would complete my objectives. I would like to thank my wife Jessica for being patient with me during my research as we had many other plans coming to be as I completed my research.
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1. Introduction

1.1 Background

Because of the abundant reserve of coal in the U.S. and worldwide, coal-based power generation will continue to play a major role in energy supply for a very long term.\textsuperscript{1, 2} Thus, developing advanced technologies for production of affordable and clean coal-derived energy is the key to securing a sustainable economic development. It is anticipated that the utilization of coal-derived synthesis gas (syngas) will continue to increase as the emerging high efficiency gas turbine, new advanced combustors/boilers, and fuel cell power systems approach the marketplace.

The performance, economics, and environmental impact of these advanced power systems are affected by the constituents in the fuel and discharge gases. Therefore, real time monitoring and prompt and proper handling of fuel variability and discharge gases are critical to the realization of the high performance clean power systems. Acquiring full knowledge of the gas streams in these energy systems will rely on a suite of sensors and sensor systems that can operate in wide ranges of physical and chemical conditions. The Electric Power Research Institute (EPRI) estimated that approximately $409 million can be saved annually in the existing fossil-fuel-based power plants in the United States by implementing advanced sensor and control technologies to achieve a 1\% increase in efficiency.\textsuperscript{11} Unfortunately, currently available sensors are incapable of operating directly in many of the locations in the energy production systems that involve high temperature, high pressure, and presence of particulates and corrosive components. Successful development of sensors applicable of functioning in such harsh conditions will entail
highly integrated research in the areas of material science, chemical engineering, and sensor technology. [3]

In the past decade, small-size fiber optic devices integrated with chemically sensitive photonic materials emerged as a new class of high performance optical chemical sensor that have the potential to meet many analytical challenges in future clean energy systems and environmental management. The fiber optic sensors (FOS) have the general advantages of chemical and thermal stability, small size, passive sensing mechanisms, remote operability, ease to construct multiplexed or distributed sensors, and insusceptibility to electromagnetic fields. Recently, our research group together with collaborators in Missouri University of Science and Technology developed zeolite-integrated optical fiber devices by growing MFI-type zeolite thin films directly on the surfaces of structured communication optical fibers such as straight cut fiber endface and long period fiber grating (LPFG). [4-8] The chemical sensing mechanisms of these zeolite-fiber optic devices is based on the change of zeolite refractive index ($n_z$) upon sorption of the analyte molecules into the zeolitic channels. [4] We have also demonstrated a proton conductive perovskite thin film coated long period fiber grating (LPFG) for high temperature hydrogen detection. [9] In this proposed research, we aim to develop a copper-doped-zirconia (CDZ) thin film coated LPFG for sensing carbon monoxide gas at high temperature and investigate the effect of the CDZ material composition on the device’s optical sensing performance.

**LPFG-Based Optical Chemical Sensors:** The LPFG is an inline fiber device with its core refractive index changing periodically to promote coupling between the core mode and the co-propagating cladding modes. [10-13] The LPFG used in this project is obtained by inscribing
periodic index perturbations into the core of an optical fiber using CO\textsubscript{2} laser irradiation.\textsuperscript{[14]} The characteristic resonance wavelength ($\lambda_R$) of a LPFG is given by the following equation\textsuperscript{[15]}:

$$\lambda_R = [n_{\text{eff}}(\lambda_R) - n_{cl}^R(\lambda_R)]\Lambda$$  \hspace{1cm} (1)

where $n_{\text{eff}}$ is the effective refractive index of the propagating guided mode, $n_{cl}^R$ is the effective refractive index of the $R^{th}$ cladding mode, and $\Lambda$ is the period of the LPFG that is normally in the range of 100-1000 \textmu m. For a given LPFG with fixed fiber and grating parameters, the $\lambda_R$ varies when the refractive index of the surrounding medium changes. This refractive index change allows LPFG-based sensors to be used for direct or indirect measurement of chemical concentrations through the change in the refractive index of the overcoat.\textsuperscript{[15-19]}

An effective way to construct LPFG chemical sensors is to coat chemically responsive photonic material on the LPFG. The coated film becomes part of the LPFG’s surrounding medium. Thus, when the refractive index of the overcoat changes upon its interaction with the analyte molecules, $\lambda_R$ varies accordingly and the shift of $\lambda_R$ can be used to quantify the analyte concentration through proper calibrations. The schematic of the propagation of light through the film coated LPFG is shown in Figure 1.1.
Figure 1.1. Schematic showing cladding mode of LPFG with a film overcoat and typical appearances of input and output spectra.

The LPFG FOS response is based on the variation of LPFG transmission spectrum caused by changes in the refractive index of the overcoat. The $\lambda_R$ of the LPFG is a function of the refractive index of the overcoat that can be expressed by the following equation:

$$\frac{d\lambda_R}{dn_{ov}} = \frac{d\lambda_R}{dn_{cl,eff}} \frac{dn_{cl,eff}}{dn_{ov}}$$

(2)

where $n_{cl,eff}$ is the effective cladding refractive index. The $\lambda_R$ dependence on the $n_{ov}$ is nonlinear and the refractive index detection sensitivity is determined by the index difference between the fiber and overcoat. The current accuracy of measuring the resonant wavelength by commercial optical spectrum analyzer (OSA) or tunable lasers is down to 1 pm. With this accuracy the LPFG sensor is theoretically capable of detecting a $n_{ov}$ change of $10^{-8}$-$10^{-9}$ when the $n_{ov}$ is close to $n_{cl}$.

Doped-Ceramics As High Temperature Gas Sensing Materials: Many doped-ceramics can reversibly react with specific gases found in the coal-derived syngas and combustion gases at high temperatures. The reactions may include chemisorption of gas molecules on the surface/grain boundaries, gas dissolution into the solid phase, redox reactions in the solid structure, and gas-induced defect reactions. These interactions cause changes in material surface properties, crystal lattice parameters and density, electron states, defect population, and band gap energy, that alter the refractive index and light absorption behavior of the material. Many solid oxide materials have been utilized for their electrical and electrochemical properties. This includes the well known uses of stabilized zirconia as solid oxide fuel cell
electrolytes due to its high ionic conductivity and transference number, the perovskite-type mixed conduction oxides have been used as SOFC cathodes, and a variety of electrochemical gas sensors based on the surface electrochemical reaction. Some of the ionic solid oxides such as zirconia have also been used as optical components in the optical communication systems and it is possible that highly selective optical sensors can be constructed using these materials to detect gases by measuring the gas-induced changes of refractive index or absorption spectrum. However, optical gas sensors based on doped oxide materials have not been reported in part because of the technical challenges to integrate the chemically and optically functional ceramics with optical devices that can directly operate in high temperature (>500°C) and corrosive atmospheres.

Recently, our research group has successfully demonstrated a new LPFG-based FOS for for in situ measurement of bulk hydrogen at high temperature. The new FOS was constructed by coating the LPFG with a proton conducting perovskite oxide thin film. The perovskite-type proton-electron/hole mixed conducting oxides have the general chemical formula of $AB_{1-x}M_xO_{3-\delta}$, where A and B are metal ions commonly from the group of (Ca, Sr, and Ba) and the group of (Ce, Tb, Zr, and Th), respectively. $M$ is a dopant with a variety of choices for elements and doping level (normally $x = 0 \sim 0.2$) that significantly influences the oxygen deficiency ($\delta$), conductivity, and material chemical stability. At high temperatures, exposing these perovskite oxides to oxygen- and hydrogen- containing gases causes the following reactions in the solid phase:

\[
\text{in oxygen: } \quad V_{O}^{\ddagger} + \frac{1}{2} O_2 \xrightleftharpoons{k_1} O_{O}^X + 2h^* \tag{3}
\]

\[
\text{in hydrogen: } \quad H_2 + 2h^* + O_{O}^X \xrightleftharpoons{k_2} 2OH^* \tag{4}
\]
At high temperature, the types and population of the ionic and electronic defects in the SCZY structure depend on the surrounding hydrogen partial pressure. Thus, varying the H₂ concentration changes the SCZY film refractive index and light absorbing characteristics that in turn shifts the \( \lambda_R \) of the LPFG. The perovskite-type oxide used in our group by Tang et al.\(^9\) was Sr(Ce₀.₈Zr₀.₁)Y₀.₁O₂.₉₅ (SCZY). The SCZY nanocrystalline thin film was coated on the \( \phi125 \) µm LPFG by a facile polymeric precursor route. The SCZY-coated LPFG sensor has been demonstrated for bulk hydrogen measurement at 500 °C with very good sensitivity, high thermal stability/reversibility and H₂-selectivity over other relevant small gases including CO, CH₄, CO₂, H₂O, and H₂S, etc.

Preliminary research was also conducted in our group to explore the possibility of using zirconia-based ceramic thin film coated LPFG for CO sensing. Yttrium-stabilized zirconia (YSZ, Zr:Y=84:16) and Cu-doped zirconia (CDZ, Zr:Cu=84:16) nanofilm-coated LPFGs were synthesized by the polymeric precursor route which is similar to the procedure employed for fabricating the SCZY-LPFG sensors. The crystallite sizes in the zirconia-based ceramic films were about 10-25nm. The YSZ-LPFG and CDZ-LPFG fiber device were tested for CO sensing in a temperature range of 500 – 650°C. The YSZ-coated LPFG sensor had a low sensitivity for low concentration CO probably because of the very limited variation of oxygen vacancies in the YSZ crystal phase upon ppm-level changes in CO concentration. Very encouragingly, The CDZ-coated LPFG sensor exhibited excellent reversibility and high sensitivity to CO below 250 ppm in N₂ carrier gas as shown in Figure 1.2 (a) with a response time about 2~4 min, which was determined by the time needed for scanning of laser spectrum in a near IR wavelength region of 1510 – 1640 nm. However, the CDZ became unstable at CO concentration of 1% (Fig. 1.2 (b)).
Figure 1.2  (a) $\lambda_R$ of the CDZ-LPFG as a function of CO concentration at 550°C and (b) LPFG signal ($\lambda_R$) drifting (1% CO, air, CO$_2$) at 550°C.
1.2 Objective

The goal of this thesis research is to fabricate copper-doped zirconia nanocrystalline thin film coated long period fiber grating sensors and evaluate the sensor performance for CO detection at high temperature. The specific technical objectives of this thesis work include:

(1) To develop an effective procedure for synthesizing CDZ nanocrystalline thin films on the surfaces of optical fiber and silicon wafer, including identifying appropriate conditions for synthesis of the metal ion-chelated polyethylene glycol (MCPEG) precursor, coating the MCPEG polymeric precursor films on the fiber and silicon wafer, and thermal treatments to convert the polymeric precursor films to solid oxide thin films.

(2) To evaluate the high temperature CDZ-LPFG sensor response in $\lambda_R$ as a function of CO concentration (in N$_2$ carrier) and investigate the effect of Cu-content on the sensor sensitivity, stability, and reversibility through high temperature optical signal monitoring as well as X-ray diffraction and microscopic material characterizations.
2. Copper-Doped Zirconia Nanocrystalline Thin Film Synthesis and Characterization

The nanocrystalline thin films of the doped-ceramic materials are synthesized by the polymeric precursor route. The basic film synthesis procedure includes three steps \([37, 38]\) (i) HNO\(_3\)-catalyzed polymerization of ethylene glycol mixed with aqueous solution of metal ions to form linear metal ion-chelated polyethylene glycol (polyester) (MCPEG), (ii) coating thin films of the MCPEG by on the fiber surface brush-coating and on the silicon wafer by spin-coating, and (iii) drying (~100°C) and firing (500 – 800°C) of the polymeric precursor films to form nanocrystalline oxide films with sufficient density. The general procedure for fabricating the CDZ thin films on substrates is depicted in Figure 2.1.

**Figure 2.1.** Procedure for fabrication of the CDZ nanocrystalline film coated LPFG sensor.

The ion chelating and polymerization reactions are shown below (M denotes metal ions, i.e. Zr\(^{4+}\) and Cu\(^{2+}\) in this work). \([39]\)

\[
\begin{align*}
\text{HO-C-C=O + M} & \xrightarrow{\Delta \text{HNO}_3} \text{HO-C-C=O + M} \\
\text{HO-C-C-OH} & \xrightarrow{\Delta \text{HNO}_3} \text{HO-C-C-OH}
\end{align*}
\]

Polymerization and Chelation in presence of Metal ions
The metal ions constituting the desired doped-ceramic material are homogeneously distributed in the polymeric matrix. Up on fast calcination, the metal ions simultaneously turn into molecular species of metal oxides when the polymer chains are decomposed and burned out rapidly. This generates a large number of crystal nuclei which deposit on the fiber surface. The resultant nanocrystals experience only limited crystal growth by subsequent incorporation of the residual un-nucleated oxide molecular species at low firing temperatures. The final nanocrystallite size depends primarily on the firing temperature. Because of the instant formation of oxide crystals from a high-density homogeneous ionic mixture, homogeneous multi-ionic solid solution is obtained without a high temperature annealing process.

The polymeric precursor approach can produce dense nanofilms of multi-cation solid solution at temperatures from 500 to 800°C. The resultant nanocrystallite size increases with increasing the firing temperature. At such a low temperature the manufacturing process is particularly desirable for retaining the nanostructure, preventing solid-state reactions at the CDZ-film/SiO₂-fiber interface, and preserving the optical waveguide properties. The typical grain size of the dense films is typically in a range of 5~30 nm for firing temperatures from 500 to 800°C. The nanocrystalline structure can increase the gas diffusivities and/or ionic conductivities by as much as a few orders of magnitude compared to the bulk materials. Thus, with a thickness of ~100 nm, the nanofilm is expected to exhibit fast response and high sensitivity.
2.1 Synthesis and Characterization of Zr$^{4+}$ and Cu$^{2+}$ Chelated Polyethylene Glycol

2.1.1 Synthesis of Metal Ion Chelated Polyethylene Glycol

The polymeric precursor is synthesized through an acid-catalyzed polymerization of ethylene glycol to polyethylene glycol, which in the presence of metal ions allows for chelation of the metal ions to the oxygen molecules of the polymer chain. The following general procedure was used for all of the CDZ precursor solutions used in this research.

In a 125-ml flask, which has been cleaned using dawn soap then rinsed with DI water three times with a final rinsing of isopropanol and dried at 40°C, Zirconyl Chloride Octahydrate and Copper(II) Nitrate Hemipentahydrate are added. To the powders, 20 ml of DI water is added and the solution is stirred for 10 minutes at room temperature. Once the solution is clear and well mixed, 40 ml of Ethylene Glycol is added to the solution while stirring to ensure that the solution is homogeneous. A certain amount of glycine is dissolved into the solution and stirred for 30 minutes at room temperature. This final solution is placed into a gravity convection oven (Yamato DX300) which is preheated to 80°C. The solution is polymerized for 6 days with the mouth of the flask kept open while in the oven. The polymerized solution is then aged for 8 days at room temperature before being used to coat films on the substrates. The thus prepared precursor typically possesses a viscosity suitable for film coating for about ten days afterwards. The specific amounts to which each chemical is added is shown below in Table 1 for the different Cu-doping levels [1].
Table 1: Amounts of chemicals in starting solution for synthesizing MCPEG precursors

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<tr>
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<th>3% CDZ</th>
<th>8% CDZ</th>
<th>16% CDZ</th>
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<tr>
<td>ZrOCl$_2$*8$H_2$O</td>
<td>6.425g</td>
<td>6.250g</td>
<td>5.92g</td>
<td>5.41g</td>
</tr>
<tr>
<td>Cu(NO$_3$)$_2$*x$H_2$O</td>
<td>-</td>
<td>.1125g</td>
<td>0.3g</td>
<td>0.6g</td>
</tr>
<tr>
<td>DI water</td>
<td>20ml</td>
<td>20ml</td>
<td>20ml</td>
<td>20ml</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>40ml</td>
<td>40ml</td>
<td>40ml</td>
<td>40ml</td>
</tr>
<tr>
<td>Glycine</td>
<td>1.5g</td>
<td>1.5g</td>
<td>1.5g</td>
<td>1.5g</td>
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2.1.2 Characterization of the Polymeric Precursor

Once the polymeric precursor had been synthesized and has aged for 8 days it was then used for coating on various surfaces. The polymeric precursor was examined by an ATR FT-IR. The ATR sample stage uses a diamond crystal to collect the reflection intensity across the IR range. Solutions with varying levels of copper dopant were prepared along with the monomer as well as the polymer in the absence of the metal ions for comparison. The spectra of these samples are shown below in Figure 2.2.
Figure 2.2. FTIR spectra of various polymeric precursors at different stages of synthesis

The scanning range was from 4000 to 400 wavenumbers (cm\(^{-1}\)). The blanks prepared are ethylene glycol (EG) and poly ethylene glycol (PEG) free of metal ions. The other samples were taken from polymer solutions synthesized in the above section and used in actual film coating processes. The spectrum of each sample was shifted vertically so that the difference between each is clearly visible. There are four distinct differences in the spectra: (i) peaks at 1755 cm\(^{-1}\) for the metal incorporated polymers assigned to carbon-oxygen double bonds (:C=O), (ii) shoulders at 1640 cm\(^{-1}\) and 1540 cm\(^{-1}\) associated with the (C-O) bond adjacent to the (C=O) bond, (iii) a small peak around 1150 cm\(^{-1}\) also associated with (C-O) bond adjacent to the (C=O) bond, and (iv) shoulders around 950 cm\(^{-1}\) and 650 cm\(^{-1}\) associated with the weak interaction between the chelated metal ion and the double bonded oxygen atom (M-O). The strong peaks at around 1755 cm\(^{-1}\), which indicate carbon-oxygen double bonds in the structures of polymers, are only present in the samples taken from solutions synthesized in the presence of metal ions but not the
metal-free PEG or ethylene glycol samples which do not contain C=O double bonds. The chemical formulas of the metal ions chelated PEG (MCPEG) and pure PEG are shown below.

$$\text{PEG:}$$

$$\text{MCPEG:}$$

If the metal ions were not chelated, the structure shown above would not be stable enough to exist. The polymer chain would include only carbon hydrogen bonds and carbon oxygen single bond along with the large oxygen hydrogen bond which is seen at 3330 cm\(^{-1}\) in figure. The metal oxygen bond is seen in the IR spectrum region of 400-950 cm\(^{-1}\). This peak is very weak when there is a definite metal oxygen bond but in our case the metal oxygen interaction is very weak such that a bond is not formed so the appearance of this peak as a weak shoulder is not surprising. Furthermore the polymeric precursor solution level is marked during synthesis and originally the polymerization time at 80\(^\circ\) C was set for 3 days. The identification of precursor synthesis duration was done through the actual sensor preparation and test. The 3-day polymerized solution failed to form a continuous film due to insufficient viscosity. The polymerization time was then extended to 6 days. With the 6-day polymerization solution, uniform films were achieved and the resultant CDZ-coated sensors exhibited good sensitivity to ppm level CO. Also, after 6 days polymerization, no appreciable precipitates were observed.
Further extension of the polymerization duration to > 8 days or prolonging aging time for > 10 days resulted in large cracks in the oxide film due to large film thickness (Figure 2.3).

**Figure 2.3** Larger cracks formed in ZrO$_2$ film on fiber prepared from a polymeric precursor obtained by 8 days of polymerization and 6 days of room temperature aging.

2.2 Synthesis and Characterization of Copper Doped Zirconia (CDZ) Nanocrystalline Particles

2.2.1 Synthesis of CDZ Nanocrystalline Particles

Nanocrystalline powders were prepared to determine grain size and crystal phase by TEM and XRD characterization. All the powders were synthesized using the same firing conditions as the conditions employed for fabricating their respective sensors. All the powders were fired in air at 650$^\circ$C and annealed at 700$^\circ$C. Both the firing and annealing processes used a
heating rate of 5°C/minute and a dwell time of 30 minutes. The detailed experimental procedure is explained below.

In order to synthesize nanocrystalline powders, certain amount of polymeric precursor solution is placed into a ceramic crucible. The crucible is then placed into a furnace for firing (NEY Vulcan 3-130 or 3-550). The firing process is closely monitored due to excessive smoke which is produced from the synthesis process in the early stage of polymer decomposition. Once the powders are cooled down to room temperature, they are then subjected to an annealing step at 700°C for a dwell time of 30 minutes. The powders are then stored in a sealed container until needed for characterization or gas treatment.

2.2.1 Characterization of CDZ Nanocrystalline Particles

The crystal phase of the CDZ nanoparticles was examined by XRD. The CDZ XRD pattern is shown in Figure 2.4 together with the standard patterns of the tetragonal and monoclinic zirconia phases. Copper oxide characteristic peaks are not seen in the XRD spectrum and the CDZ material clearly has tetragonal and monoclinic phases of zirconia. This indicates that CuO is doped in the zirconia structure forming solid solutions.
Figure 2.4. XRD pattern of the CDZ nanocrystalline particles (M – monoclinic and T – tetragonal)

In order to determine the size of the primary crystallites, the as synthesized CDZ particles (Cu to Zr atomic ratio of 16:84) were examined by high resolution TEM. Figure 2.5 shows the TEM images of the as synthesized CDZ particles with no further thermal treatment and those after further annealing at 550°C for 48 hours and 96 hours, respectively. The images show that the as-synthesized CDZ nanograins had a size distribution of about 10 nm to 25 nm; the thermal treatment at 550°C did not cause obvious grain growth but appeared to make the grain size more uniform likely due to the well-known Ostwald ripening effect. [44] The grain size and morphological thermal stability of the CDZ nanoparticles is desirable for developing CDZ-coated FOS for high temperature applications. Also, the 16% Cu-doped CDZ grain size was found to be similar to the sizes of pure zirconia, 3% Cu-doped and 8% Cu-doped CDZ nanoparticles prepared by the same procedure under identical conditions.
Figure 2.5. TEM images of CDZ nanocrystalline particles (A) as-synthesized, (B) after annealing at 550°C for 48 hours, and (C) after annealing at 550°C for 96 hours.

2.3 Synthesis and Characterization of Copper-doped-Zirconia Thin Films on fiber and Silicon Wafer

2.3.1 Coating Copper-doped-Zirconia Thin Films

CDZ thin films were coated on silicon wafers and polished sapphire chips for measuring refractive index and electrical conductivity, respectively. The polymeric precursor solution, i.e. MCPEG obtained in previous section, is coated on a 2cm×2cm silicon wafer by spin-coating method. The spin coating of polymeric precursor films was performed in a Labconco Horizontal bench-top clean room (Purifier Series). The bench-top clean space was allowed to purify the air and surface for 1 hour prior to the film coating.
The silicon wafers were first cleaned by DI water in ultrasonic bath for 10 minutes and then wiped thoroughly with powderless lab tissues soaked with isopropanol. The cleaned silicon wafer was used immediately after removing the isopropanol from the surface. The sapphire substrates (2.5cm × 2.5cm squares with one side polished) were purchased from Crystal systems Inc. MA. The sapphire wafers are individually stored in vacuum-sealed bags and are free of contaminants prior to opening, therefore no cleaning was needed.

The polymer films were coated on the silicon and sapphire wafers using a two-stage spin coater (Chemat Technology Spin Coater KW-4A). The spin coating process was done by two continuous steps: step 1 was set to 500 rpm for 15 seconds and step 2 was set to 2400 rpm for 50 seconds. The two-step coating process is used to ensure that the entire surface of the substrate is wetted by precursor during the first step of low-speed spinning and a uniform thin film is formed by the second step of high-speed spinning. After the spin coating process, the MCPEG film-coated chip is placed on a hot plate (Chemat Technology Hot Plate KW-4AH) for 1 minute to dry the thin film (i.e. to expel residual water and volatile components in the polymeric films), at a temperature of 100 – 120 °C. The dried films on the substrates were then placed on the hot plate at 300°C for 1 minute to quickly remove any excess monomer and polymer.

The supported film samples were then placed in a furnace (NEY Vulcan 3-130 or 3-550) for the firing process. The firing process heats the sample to 650°C at a fast rate of 5°C/minute and has a dwell time of 30 minutes before cooling down at cooling rate of 5°C/min. The coating-drying-firing cycle was repeated to achieve various thicknesses of the nanocrystalline oxide films. Once the coating process was complete the film sample received a final thermal shock treatment/annealing step at 700°C for 30 minutes with rapid heating and cooling rates of 5°C/min.
2.3.2 Characterization of the Thin Films on Flat Substrates

The CDZ thin films coated on silicon wafers were tested by high resolution SEM to examine the morphology, integrity, and thickness of the films. Figure 2.6 shows the SEM pictures of 16% Cu-doped and 8% Cu-doped CDZ films on silicon wafer obtained by five times spin coating. The thicknesses of the two CDZ films with different Cu contents are nearly the same which is about 125 nm. The films appeared to be quite dense and uniform in thickness without and cracks in all locations randomly scanned during SEM sampling/imaging.
Figure 2.6. SEM pictures of the cross-sections of silicon wafer supported CDZ films obtained by five times of coating: (a) 16% Cu-doped and (b) 8% Cu-doped

The refractive index of the 16% Cu-doped CDZ thin film shown in Figure 2.6 (a) was measured by ellipsometry. The CDZ film refractive index is presented in Figure 2.7 as a function of wavelength. This refractive index is close to 1.51, which is greater than the refractive index of the fiber (1.45), and fairly constant in the wavelength range of 1510 – 1640 nm, decreasing slightly from 1.523 at 1510 nm to 1.509 at 1640 nm.
Figure 2.7 The refractive index \((n)\) and extinction coefficient \((k)\) of the 16% Cu-doped CDZ film coated on the silicon wafer.

2.4 Coating CDZ Thin Film on LPFG

The LPFG is manufactured by our collaborators at Missouri University of Science and Technology (MST). The LPFG was fabricated using point-by-point CO\textsubscript{2}-laser irradiation in a single mode silica fiber (Corning\textsuperscript{®} SMF-28\textsuperscript{TM}), which has a φ9-μm Ge-doped core and a φ125-μm fused silica cladding.\textsuperscript{[14]} The grating segment has a total length of ~50 mm and a \(\Lambda\) of 520 μm. This LPFG exhibited long term stability at 550 °C with only a small thermal drifting of ~1.9 nm over 200 h and could survive at 800 °C for between one hour and a few hours before the resonant peak disappeared. The thermal instability at high temperature is caused by annealing of
the laser-inscribed gratings in the core that leads to the disappearance of the periodical variation of refractive index.

In order to coat uniform polymeric precursor films on the LPFG, the fibers are cleaned using isopropanol. Typically at least three LPFGs are horizontally mounted (suspended) in tubular furnace (Thermo Electron Corporation Lindberg Blue/M Tube Furnace) and only one LPFG is spliced to a tunable laser for monitoring the synthesis of the sensor. The blank LPFGs suspended through the center of the tubular furnace received a preliminary firing step, in which the furnace is heated to 650°C at a rate of 5°C/minute with a dwell time of 30 minutes. This firing step is performed to ensure that there is no isopropanol and other adsorbed contaminants left on the fiber from the cleaning step. The fibers are then cooled to room temperature for coating the precursor films.

The LPFG transmission spectrum is collected after each step of sensor preparation: blank LPFG after being installed, blank LPFG after firing, after applying each coating, and after firing each precursor coating. The film coating process is as following: A fine tip brush is saturated with the polymeric precursor solution enough to form a droplet on the end of the brush. The droplet is then placed on the blank LPFG and is pulled along the fiber at a slow rate of about 15cm/minute. This is repeated 4 times which represents sub-coating 1. A spectrum is collected to determine the effect of the precursor coating on the resonance wavelength peak. The polymer solution coating on the fiber is allowed to dry at room temperature for 10 minutes before the next sub-coating begins. The previous coating procedure is repeated three times. The LPFG is fired under the same conditions as that used for the initial firing for the blank fiber. This is repeated until the desirable film thickness is acquired. Figure 2.8 shows a polymeric solution droplet put on a fiber tip and the film formed after dried at 100°C.
For all of the sensors reported in this thesis the polymeric precursor was coated 4 times which results in an oxide film thickness of about 200nm. This is a thickness which ensures that the entire grating is coated with a uniformly thick and dense film. Once the sensor has been coated the desired number of times, a final annealing or thermal shock step is conducted at 700°C heating at a rate of 5°C/minute with a dwell time of 30 minutes. The thermal shock treatment is performed in order to stabilize the material microstructure and grain size for operation at 550°C.

Figure 2.9 (a) shows the typical SEM images of the single-time coated polymeric precursor film on the fiber with a uniform thickness of ~ 0.5 μm. Figure 2.9 (b) and (c) show cross section and surface of the four-time coated CDZ film on the fiber after final annealing at 700°C for 30 minutes. The four-time coated CDZ film on the fiber has a thickness of ~250nm. A low magnification SEM picture is also given in Figure 2.10 to show the excellent integrity of the CDZ film without any visible cracks or uncovered areas.

**Figure 2.8.** Optical microscopic pictures showing the drop sliding (left) and dried CDZ polymeric precursor coating (right) on the surface of the optical fiber end.
Figure 2.9. (a) Cross-section of the polymeric precursor-coated LPFG, (b) SEM picture of the CDZ nanofilm (cross-section) and (c) the SEM picture of the CDZ film surface on LPFG.

Figure 2.10. Low magnification SEM picture of a 16% Cu-doped CDZ film (4-time coated) on the fiber surface.
3. Evaluation of the CDZ-LPFG Sensors for CO Detection at High Temperature

3.1 Apparatus and Data Processing

Experimental apparatus: The high temperature gas sensing tests are performed using an apparatus shown below in Figure 3.1, which is similar to that described in a previous publication [5, 9]. The sensor test system consists of three units: (i) the gas supply unit, (ii) the gas chamber hosting the sensor, and (iii) source laser and signal acquisition/processing unit.

![Figure 3.1. Schematic diagram of the high temperature optical sensor testing system](image)

The CDZ-coated LPFG segment was housed in a test chamber made from a ¼”–I.D. stainless steel tube. The sensor-mounted ¼” SS tube is placed horizontally in a tubular furnace (±1.0 °C, Thermo Electron Corp Model Lindberg Blue/M Tube furnace). The two ends of the tube are connected to the sample gas supply unit and ventilation, respectively. The LPFG transmission spectrum was obtained in a near IR wavelength range from 1510 to 1640 nm by sweeping the wavelength of a tunable laser (Agilent 81640A) and detecting the light using an
optical power detector (Agilent 8164A) coordinated with a computer data acquisition system. In all measurements, a low flow rate of the sample gas (10 cm$^3$ (STP)/min) was used to ensure that the gas reached the set temperature when contacting the sensing element. For safety assurance, a household CO detector is installed near the sensor testing apparatus.

**Sensor response ($\Delta \lambda$):** In the gas sensing test, N$_2$ is used as the carrier gas and the baseline of the CDZ-LPFG optical response was measured in pure N$_2$. The baseline $\lambda_{R,N_2}$ is given as a function of temperature. $\lambda_{R,N_2} = \lambda_{R,N_2}^0 + \zeta T$, since the $\lambda_R$ of a LPFG is known to exhibit excellent linear dependence on temperature. The $\zeta$ values are typically around 0.1 nm/$^\circ$C with small variations among different CDZ-LPFGs. Thus, the gas sensing signal at a specific temperature, which is the shift of $\lambda_R$ in response to switching from N$_2$ to an analyte gas “$i$” ($\Delta \lambda_{R,i}$), is given by:

$$\Delta \lambda_{R,i} = (\lambda_{R,i} - \lambda_{R,N_2})_T$$

(8)

where $\lambda_{R,i}$ is the resonant wavelength in gas $i$ at temperature $T$.

The sensor reversibility and response speed of the CDZ-LPFG in gas sensing is studied by measuring the single wavelength intensity as a function of time when the gas stream is switched between air and a CO/N$_2$ mixture. The response time is represented by the time required for stabilizing the output light intensity at the fixed wavelength. The particular single wavelength is specifically chosen at each temperature for high sensitivity.
3.2 CDZ-LPFG Sensor Response to CO at High Temperature

3.2.1 Single Wavelength Response to CO

The four-time coated CDZ-LPFG sensors synthesized are mounted in the sensor test tube. Once the sensor was mounted and pulled tight to ensure no bending within the tube, the sensor was then tested for response. Bending or strain on the LPFG has been shown to induce a response \cite{45} in transmission intensity. This is why the fiber is mounted in the test tube then gently pulled tight on either end to minimize specific errors. Tests of single wavelength response to CO at 550ºC were performed for CDZ-LPFG sensors with various Cu doping levels, including 0% Cu (i.e. pure zirconia), 3% Cu, 8% Cu, and 16% Cu, respectively. The test was conducted by switching the feed stream between air and mixtures of CO and N\textsubscript{2} with varying CO concentration. In order to determine which single wavelength the test will be performed at a spectrum is taken to locate the resonant wavelength. Once the resonant wavelength is found the single wavelength is chosen so that it is to the left side of the peak by ~ 7 nm. For the single wavelength data a data point was collected every 3 seconds. Each collected data point is an average of 10 measurements taken by the instrument. This ensures the accuracy of the reading.

Figure 3.2 shows the results of the single wavelength responses to CO at 550ºC for the three sensors coated with CDZ films of different Cu-dopant concentrations. All three sensors exhibited reversible responses to the switch between air and CO-containing N\textsubscript{2} gases. It should be noted that the response in transmission light intensity to switching atmosphere at each CO concentration was reproducible as shown by the repeated data at 500 ppm and 1,000 ppm CO on the 3% Cu-doped CDZ-LPFG in Figure 3.2 (b). It was observed that the single wavelength response (i.e. change in intensity) increased with increasing the CO-concentration for all three
sensors that demonstrates the feasibility for the sensors to quantitatively detect CO in the gas stream at high temperature. Another important finding on the sensor response is that sensor’s response time is very different for oxidizing gas (air) and reducing gas (CO/N₂). For all sensors the response time to CO, which involves reduction of Cu²⁺ to Cu⁺, was typically 20 – 30 minutes, while the response time to air, which involves oxidation of Cu⁺ to Cu²⁺, was less than 2 minutes. In each of the figures below the arrow points to what time that air was switched to as the feed stream (In Air = Switch to Air as the Feed stream). As can be seen in figure 3.2(d) the 16% CDZ-LPFG lost reversibility when exposed to higher concentrations of CO resulting in a rather small response to 1% CO. This unexpected irregular response suggests CDZ material stability under high CO concentration.

(a) Pure ZrO₂-LPFG response at λ=1558 nm
(b) 3% Cu-doped CDZ-LPFG response at $\lambda=1559$ nm

(c) 8% CDZ-LPFG response at $\lambda=1562$ nm
(d) 16% CDZ LPFG response at λ=1576nm

Figure 3.2. Single wavelength response of the CDZ-LPFG sensors to switch between air and N₂-carried CO with various concentrations.

3.2.2 Sensor Output ($\Delta \lambda_R$) as a function of CO concentration

All of the CDZ sensors were tested using the apparatus schematically shown in Figure 3.1. Once the sensors were mounted in the ¼" OD stainless steel tube the programmable furnace was heated to the specific temperature of the test and allowed to stabilize at that temperature for 2 hours before the test began. In experiments of testing sensor output ($\Delta \lambda_R$) as a function of CO concentration, sufficient time was allowed for the optical output signal to stabilize, typically 35 minutes for the reduction reaction (after introducing a specific concentration of CO) and 10 minutes for the oxidation reaction (after introducing air to the system). The stabilization time is determined at which no appreciable shift of $\lambda_R$ is observed in 10 minutes, excluding the thermal
drifting which is insignificant compared to the CO-caused shift. Multiple spectra were taken waiting 5 minutes between each spectrum to monitor and ensure that gas-induced change of the CDZ film property is equilibrated.

Figure 3.3 presents the results of CO sensing for sensors with Cu doping level of 0% (pure ZrO$_2$), 3%, 8%, and 16%. The results show excellent quantitative correlations between the sensors’ outputs and the CO concentration at ppm levels for all four sensors. This demonstrates that the sensors are capable of quantitatively measuring the low concentration of CO at high temperature, e.g. 550°C.

The general trends of the curves of each of the compositions give are similar with a large slope, namely high sensitivity, initially for low CO concentration and then a flattening off at higher CO concentrations. The change in copper dopant content from 0% up to 16% clearly affects these general trends mostly affecting the initial slope and the CO concentration at which the plot begins to plateau.
(a) ZrO$_2$-LPFG sensor

(b) CDZ-LPFG with 3% Cu
(c) CDZ-LPFG with 8% Cu

(d) CDZ-LPFG with 16% Cu
Figure 3.3. Optical responses in $\Delta\lambda_R$ at 550°C as a function of CO concentration for sensors with different Cu-doping levels.

Figure 3.3 (a) shows the concentration dependence of the ZrO$_2$-LPFG sensor response to CO from 100 ppm CO to 5% CO. As can be seen the initial slope is very sharp and quickly levels off at about 10,000 ppm. The sensor response is likely caused by the change of oxygen vacancy population under different CO concentrations since the CO concentration determines the O$_2$ partial pressure by the following reaction equilibrium:

$$CO + \frac{1}{2}O_2 \leftrightarrow CO_2$$

(9)

In the presence of CO, i.e. low O$_2$ partial pressure, oxygen is extracted from the solid oxide leaving two electrons at the O site. These two electrons are readily excited to conduction band as described by the following reaction $^{[46]}$:

$$O_o^x \leftrightarrow \frac{1}{2}O_2(gas) + V_{o}^{**} + 2e^-$$

(10)

The results indicated that the above reaction-induced change of chemical and optical properties in the pure zirconia phase is limited at relatively low temperature of 550°C and hence the sensitivity is low.

The CuO doping into the zirconia phase increases the oxygen vacancy population ($CuO_{zr} \rightarrow Cu_{zr}'' + V_{o}^{**} + O_2^X$) and the Cu$^{2+}$ is more readily reduced in CO-containing gas to cause greater changes in material properties as compared to pure ZrO$_2$:

$$CuO + CO \leftrightarrow Cu_2O + CO_2$$

(11)

Compared to the pure zirconia coated LPFG, the CDZ-LPFG containing Cu dopant obviously had much enhanced sensitivity to CO as indicated by the significantly greater $\Delta\lambda_R$ in
response to the same CO concentration in Figure 3.3 (b), (c), and (d). This suggests that the Cu-doped CDZ-LPFG is able to detect lower concentrations of CO than the pure ZrO$_2$-LPFG due to the involvement of Cu$^{2+}$$\leftrightarrow$Cu$^+$ Red-Ox reaction and the increase in the concentration of oxygen vacancy caused by the copper dopant.

Based on the above results and discussion, one might expect the sensitivity of the CDZ-LPFG sensor to increase with Cu content because the solid state reactions are thermodynamically favored with large concentration of Cu$^{2+}$ reactant. However, as shown in Figure 3.4, the sensor’s sensitivity did not show a clear trend of enhancement by increasing the Cu content in the CDZ phase in the tested range of CO concentration. In general, the CO detection sensitivity, which can be measured by the absolute value of $\Delta \lambda_R$ for a given CO concentration, is much higher for the 16% Cu doped CDZ-LPFG than for the 3% Cu doped sensor at CO concentration <100ppm. However, the $\Delta \lambda_R$ output of the 16% Cu sensor appeared to level off quickly after CO concentration reached 200 ppm while that of the 3% Cu sensor kept increase almost linearly. Thus, the 3% Cu doped CDZ-LPFG exhibited higher sensitivity for CO concentrations above 250 ppm.

This suggests that a greater Cu-content in the CDZ film offers higher CO sensitivity at low CO concentration but a lower Cu-content allows for larger measuring range. The optimal Cu doping level may be obtained by balancing the sensitivity and measuring range of CO concentration depending on the specific applications. It was also observed on the 16% Cu-doped CDZ-LPFG that the sensor lost reversibility in atmospheres with CO concentration above 1%. The cause of the instability of the CDZ sensing material will be investigated in the next section.
Figure 3.4. Response comparison at lower concentrations
4. Effect of CDZ Material Stability on Sensor Performance

During the test of sensor performance, excellent sensor response reversibility was achieved for CO concentrations below 1,000 ppm on all sensors with different Cu doping levels. However, irreversible response was observed on the 16% Cu-doped CDZ-LPFG sensor at 550°C in gases with CO concentration of >1%. Figure 4.1 shows the single wavelength responses of the 16% Cu-doped CDZ-LPFG to switch between air and CO-in-N₂ with different concentrations. The sensor exhibited very good reversibility at 550°C when switching between air and 1,000 ppm CO but exhibited irregular and irreversible response after exposed to 3% CO. To find out the cause of such sensor instability in the high concentration CO, experiments have been performed to investigate the changes in chemistry and microstructure of the CDZ material after contacting CO at high temperature.

(a) Reversible response to switching between air and 1,000 ppm CO (\(\lambda = 1601\) nm)
(b) Irreversible response after exposed to 3% CO ($\lambda = 1598$ nm)

**Figure 4.1.** Single-wavelength response of the 16% Cu-doped CDZ-LPFG to CO of different concentrations.

**4.1 XRD Examination on CDZ Materials after Different Thermal Treatments**

The sensitive response of the CDZ-LPFG sensors to CO at high temperature is largely attributed to the partial reduction of Cu$^{2+}$ to Cu$^{+}$. Reversible sensor response requires that the reduction reaction does not cause crystalline phase changes in the CDZ. CDZ material stability in the CO atmosphere was examined using 16% Cu-doped CDZ nanocrystalline particles. The powder sample was created from the 16% CDZ polymeric precursor as explained previously in the synthesis section of this thesis. The powder samples were treated in the sensor testing gas at 550$^\circ$C. The thermal treatment of the CDZ powders was done by packing the powders in a 1/8” stainless steel process tube where the sample was subjected to different gas flows at 550$^\circ$C. After
the thermal treatment in different gas flows, the CDZ powders were recovered and examined by XRD.

Figure 4.2 presents the XRD patterns of the 16% Cu-doped powders before and after being treated with CO/N₂ gas mixtures with CO concentration of 1%. The sample was treated in the 1%-CO flow for 2 hours at 550°C before being cooled down in the same CO atmosphere. The main peaks shown are for ZrO₂ of different crystalline phases, namely tetragonal and monoclinic. There is a peak at 43.15 degrees (2θ) that is only present when the sample was treated with a higher concentration of CO. This peak matches the peak of Cu metal at <111> plane as shown in the reference XRD spectra in Figure 4.2 (b). Another major peak of Cu, i.e. (200) plane, is overlapping with the ZrO₂ peaks.
Figure 4.2. XRD patterns of (a) the 16% Cu-doped CDZ powders before and after thermal treatment in CO/N₂ mixtures, and (b) standard XRD pattern of Cu metal (M – monoclinic and T – tetragonal)

A separate experiment was conducted to investigate the 16% Cu-doped CDZ powders in different gases containing N₂, CO, and CO₂ at 550°C. The inclusion of CO₂ is for the potential applications of the CDZ-LPFG sensors in monitoring combustion gases. The results indicate that Cu was not formed in the 400 ppm-CO gases and again formed in the 1% CO gases with or without CO₂. The XRD peak of Cu disappeared after the sample was re-fired in air as Cu is oxidized to CuO, which can still be present in the grain boundaries and be further oxidized or reduced when exposed to respective atmospheric conditions.
Figure 4.3 (a) fresh CDZ annealed at 700 °C (b) 2 h in 400 ppm CO in N₂/CO₂ (c) 1 hr in air (d) 2-cycles between 400 ppm CO and air (e) 2 h in 1% CO in N₂+CO₂ (f) 3 times switch between 1%CO and air (g) 2 h in air for. (M – monoclinic and T – tetragonal)
Figure 4.4 the 3% CDZ Powders tested before and after similar treatment of the 16% CDZ powders (M – monoclinic and T – tetragonal)

The appearance of metal Cu as evidenced by the XRD peaks in Figure 4.2 (a) and Figure 4.3 suggests over reduction of Cu$^{2+}$ to Cu$^{0}$ in the high concentration CO/N$_2$ gas at 550°C:

$$\text{Cu}^{2+} \rightleftharpoons \text{Cu}^{+} \rightleftharpoons \text{Cu}^{0} \; (\text{metal})$$  \hspace{1cm} (14)

The strong peak of metal Cu also implies that Cu metal has likely migrated and segregated from the CDZ crystal to the grain boundaries. The lack of a strong Cu peak in Figure 4.4 shows that with lower dopant levels of Cu$^{2+}$ over reduction did not occur at the CO concentrations which were tested.

An attempt was made to identify the Cu particles using high resolution TEM. The HR TEM images of the CO-treated and untreated 16% Cu-doped CDZ particles are presented in Figure 4.5 together with the electron diffraction patterns. The Cu particles themselves could not be seen in the TEM pictures but there was an obvious difference in crystallinity between the treated and untreated powders. The untreated sample seemed to be more crystalline as evidenced by the clear atomic alignment throughout the particles and strong electron diffraction patterns typical for a multiphase nanocrystalline material.

The CO-treated sample appeared to becoming more amorphous because only some small crystalline islands were seen in the TEM image and electron diffraction pattern also diminished. This change in the crystalline structure is likely due to the over reduction of the large amount of Cu$^{2+}$ to Cu$^{0}$ in the CDZ lattice and the segregation of Cu metal to the grain boundaries that caused collapsing of the lattice nanostructure.
Figure 4.5 (A) Untreated fresh 16% CDZ powder (B) Electron diffraction pattern of untreated 16% CDZ powder (C) CDZ powders treated with 1% CO for 2 Hours (D) Electron scattering pattern of the treated CDZ powder.
5. Conclusion

Through this research, an effective procedure has been developed for synthesizing Copper-Doped-Zirconia (CDZ) nanocrystalline thin films on the surfaces of long-period fiber gratings (LPFG) to construct fiber optical sensors for high temperature CO sensing. The research identified operating conditions for synthesis of the metal ion-chelated polyethylene glycol (MCPEG) precursor, for coating the MCPEG polymeric precursor films on the fiber and silicon wafer, and for thermal treatments to convert the polymeric precursor films to solid oxide thin films. The fabricated CDZ-LPFG sensors have been tested for their responses by examining $\lambda_R$ as a function of CO concentration (in $N_2$ carrier) and investigating the effect of Cu-content on the sensor sensitivity, stability, and reversibility. The results show that the CDZ-LPFG sensors have the potential for high temperature detection of CO, particularly for low concentrations of CO.

Many findings were realized while conducting research on this thesis. While trying to determine the specific conditions for a suitable precursor different polymerization and ageing times were tested. The findings suggested that a polymerization time of less than 6 days at 80°C yielded a film that was not completely uniform therefore did not yield a response to CO. This was clear during the single wavelength response test as well as visually by SEM. An ageing period of 8 days provides for a suitable viscosity for the coating process for both thin films on the silicon wafers as well as the cylindrical LPFG surface. This precursor was found to remain suitable for film coating for another 10 days without apparent precipitates from the clear solution. The firing procedure was also optimized and found that a firing step at 650°C combined with a 30 min annealing step at 700°C was able create uniform crystallite size of 20-25nm. The thus obtained CDZ-LPFG was found to have good stability for operation at 550°C.
The CDZ material examined in this research is highly crystalline which makes it ideal for optical application. From the XRD patterns the highly crystalline CDZ material is comprised of two phases Tetragonal and Monoclinic. The crystalline phase does vary slightly between different compositions. The 16% CDZ material appears to have more of the Monoclinic phase then that found in the 3% CDZ which appears to be mostly Tetragonal. Along with the crystal phases the crystal size was observed and expected to remain consistent with other findings associated with this method for generating solid oxide films with a firing temperature between 500°C and 800°C. The film thickness of the CDZ film using the spin coating process on silicon wafer as the substrate was around 30-35 nm per coating while the films coated on the LPFG cylindrical surface done by a brush coating or slip casting method yielded a thickness of 40-50 nm per coating.

The mechanism for CO sensing is an oxidation reduction reaction between the film and the analyte gas CO. The pure Zirconia composition, the CO or reducing gas extracts oxygen ions from the film due to reduction of metal oxide. This explains the pure Zirconia sensors low sensitivity. Each of the other sensor fabricated 3, 8, and 16% Cu dopant level, the mechanism follows the oxidation reduction reaction between the different electron states of Cu. Copper was added under expectations that the response to CO would be enhanced. The sensitivity of the sensors was enhanced with the addition of Cu as a dopant however other instabilities became prevalent.

Although sensitivity was enhanced the stability and reversibility of the sensors decreased with an increase in the Cu dopant level. The pure ZrO₂ sensor had excellent stability and reversibility but lacked sensitivity to changes in CO concentration in the ppm range. Also the pure ZrO₂ sensor quickly leveled off and was unable to detect any further change in CO
concentration (with reversibility) over 1000 ppm CO. Different compositions exhibited different responses pertaining to sensitivity, reversibility, and stability. The 3% CDZ composition sensor exhibited excellent reversibility and stability but followed a similar sensitivity in the lower concentration ranges as the pure zirconia sensor. The 8% CDZ exhibited reversibility and slightly less stability as the 3% CDZ composition. The 16% CDZ composition sensor exhibited the highest sensitivity at the lower concentrations of CO <250 ppm of all the sensor compositions tested. Although the 16% CDZ sensor had the highest sensitivity, the reversibility as well as the stability became an issue when the concentration began to increase towards a concentration of 1% CO.

The XRD studies examined in Chapter 4 uncovered the presence of Cu$^{0}$. The clear peak located at 43.15° 2θ in figures 4.2 (a) and 4.3 shows the <111> face of pure Cu metal. This is evidence of over reduction of Cu$^{2+}$ to Cu$^{0}$ metal from within the crystal structure of these specific CDZ compositions. The results of HR TEM test show clear lattice fringes of the untreated sample which exhibits high crystallinity as seen in the electron diffraction pattern of the imaged sample. The 1%CO-treated sample shows only distributed crystalline domains with size of ~ 5nm where lattice fringes can be seen but large part of the material appears to be more amorphous. The evidence from both of these characterization methods lead to the conclusion that the Cu$^{2+}$ ions were being over reduced to Cu$^{0}$ metal. The Cu$^{0}$ metal then precipitated out of the CDZ lattice structure forming precipitates in the grain boundaries. The CDZ stability in CO can be improved by reducing the Cu doping level. For the same concentration of CO no Cu$^{0}$ metal was observed with the 3% CDZ composition. However, lowering Cu doping level decreased detection sensitivity for low CO concentrations.
The results of this research indicate that Cu content in the CDZ should be optimized based on the sensor application requirement: a high Cu-doping level is desirable for low concentration CO detection (e.g. low ppm level) but not suitable for bulk CO measurement; a low Cu content may be used for sensing CO of high concentration but may not be sensitive enough for detecting ppm level CO.
6. References Cited


