Fabrication of a thin double-layer thermistor based on DVB-modified polymer-derived SiCN ceramics

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A B S T R A C T

Polymer-derived ceramics (PDCs) are considered to be promising candidate materials for high-temperature sensor applications. Even though the PDCs have been studied for decades, the reliable PDC-based thin film sensors have not been produced, because ceramic films are too fragile to be handled without a substrate, but the huge shrinkage during polymer-to-ceramic conversion makes it difficult to fabricate PDC-based sensing elements on conventional substrates such as Al2O3. In this study, a thin polymer-derived ceramic double-layer thermistor was developed, using a layer with a lower resistivity as the sensing element and a layer with a higher resistivity as the substrate. The difficulty in PDC-based film sensing elements fabrication on a substrate was consequently resolved, because both the sensing elements and the substrate sustained a similar shrinkage during pyrolysis. The proposed double-layer thermistor was fabricated through step-growth photopolymerization and co-pyrolysis of two similar polymer precursors: commercially available polysilazane for the high-resistivity substrate and DVB-modified polysilazane for the low-resistivity sensing part. The DVB-modified polysilazane showed a similar shrinkage during pyrolysis, whereas the resistivity of the pyrolytic product was five orders of magnitude lower. The obtained thermistor exhibited a negative temperature coefficient in the temperature range from the room temperature to 650 °C, and the resistance of the thermistor decreased smoothly as the temperature increased. The resistance-to-voltage conversion was conducted with a voltage divider equipped with a fixed resistor and the output voltage was observed to increase smoothly along with temperature. The current sensor configuration based on PDCs was reported for the first time, and is much closer to applicable sensors.

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1. Introduction

Polymer-derived silicon-based ceramics (PDCs), such as SiCN and SiBCN, are considered for high-temperature sensor applications, due to the corresponding good functional properties at high temperatures, such as semi-conducting behavior [1,2], and piezoresistivity [3], as well as the corresponding excellent chemical and mechanical properties, such as high thermal stability [4], good oxidation/corrosion resistance [5,6], and creep resistance in extreme environments [7]. Furthermore, the unique direct polymer-to-ceramic transition process allows for attractive patterning options, such as photopolymerization and soft lithography, making PDCs a promising candidate material for high-temperature micro-electromechanical systems (MEMS) [8–10]. Temperature sensors are one promising application of PDCs (as a thermistor), built upon the corresponding semi-conducting behavior. Usually, a thermistor is required to be made quite small for high-response and high-sensitivity peculiarity to be achieved. Ceramics, although good candidate materials, are significantly fragile compared to other materials. Consequently, ceramic micro-sensor components are usually mounted to substrates to make sure that they are safe to handle. Though PDCs have been studied for decades, reliable PDC-based thin film sensors have not been produced, due to difficulty in PDC films fabrication on conventional substrates. This occurs due to the huge shrinkage of the PDCs (up to ~40%) during the polymer-to-ceramic transition process and the significant thermal stress that might occur between the substrate and the PDC film.

One way to solve this problem is to eliminate the shrinkage, in
order to obtain a near-net-shape polymer-to-ceramic transition. This can, for instance, be accomplished through the addition of fillers to the polymer precursor, as demonstrated by Greil et al. [11]. Jung et al. [12] successfully fabricated PDC-based resistance-temperature detector (RTD) arrays on quartz wafers through the addition of active fillers to the polysilazane. Still, with consideration to the resultant thermal stress from the various coefficients of thermal expansion, a safe bonding between the PDC component and the substrate could not be ensured through this approach, since the adhesion is not sufficient. Especially, this occurs when the device is operated at high temperatures.

Another way is to totally alter the configuration of the conventional film ceramic sensors by changing the mounting substrate. As it was demonstrated earlier [13], one advantage of PDCs utilization, is that the properties of PDCs could vary over a wide range through the synthesis or modification of preceramic precursors with various compositions and structures. For instance, the electrical conductivity of PDCs prepared from various polymer precursors under various pyrolysis conditions could vary by up to 15 orders of magnitude. Taking advantage of this, PDCs with different resistivity values, whereas with similar shrinkage can be prepared. The PDCs with a low resistivity can be used as sensor elements, while the PDCs with a high resistivity as substrates. Through step-growth photopolymerization, the sensor element and the substrate can be cross-linked and solidified together, producing a whole body. Subsequently to pyrolysis, a microsensor component consisting of two different layers can consequently be obtained. These layers are connected together by chemical bonds and the corresponding similar coefficients of thermal expansion ensure the stability at high temperature.

The two key elements of this strategy are: (1) the thermopyrolysis process, which requires the two precursors to sustain a similar shrinkage during the polymer-to-ceramic transition and shrink simultaneously, and (2) the resistivity, which requires the two derived ceramics to present a significant difference in resistivity. In previous studies, it was demonstrated that the free carbon played a quite important role in determining the electrical properties of PDCs [14,15]. The electrical conductivity could be adjusted through the content, distribution, and graphitization level alterations of the free carbon in the PDCs. To simplify the research, the conductivity of silicon carbonitride (SiCN) was selected to be increased, through the addition of a carbon source precursor to a commercially available polysilazane (PSN). The modified ceramics were utilized as sensing elements, whereas the unmodified ceramics were utilized as substrates for this strategy to be demonstrated. Divinylbenzene (DVB), as a widely utilized carbon source precursor [16,17], was used in this study. The effect of the addition of DVB on the thermal behavior of the modified polysilazane, which was of great importance to the double-layer structure synthesis, was characterized through Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), as well as shrinkage analysis. The chemical composition and free carbon structure of the derived ceramics, which were crucial to the resistance-temperature dependence, were analyzed through elemental analysis and Raman spectroscopy, respectively. Two ceramic layers with similar shrinkage during pyrolysis, whereas with a significant difference in resistivity of up to 5 orders of magnitude, were obtained and could be fully pyrolyzed into a whole body without crack formation. Finally, in this study, a thin double-layer thermistor prototype was successfully fabricated with this step-growth photopolymerization strategy and tested from the room temperature (RT) to 650 °C.

2. Experimental procedure

2.1. Materials and fabrication methods

In this study, a commercially available polysilazane (PSN, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China) was selected as the SiCN precursor, DVB (Sigma-Aldrich, United States) was utilized as the carbon source to improve the conductivity of SiCN, and Phenylbis (2,4,6-trimethylbenzoyl)phosphine oxide (BAPO, Sigma-Aldrich, United States) was used as the photo-initiator. The effect of DVB amount on the shrinkage of modified precursor was studied in Ref. [17]. The results demonstrated that the shrinkage during pyrolysis increased as the DVB content increased. 20 wt% of DVB addition produced a similar shrinkage compared to the unmodified precursor, while 40 wt% of DVB addition or higher, resulted in significant difference in shrinkage. Therefore, 20 wt% of DVB was selected in this study. Firstly, 20 wt% of DVB was added to the PSN and magnetically stirred for ~2 h at room temperature at 400 rpm, to form a homogeneous mixture (labeled as PSN-DVB). Consequently, 4 wt% of BAPO was added to the PSN-DVB and the pure PSN, respectively, followed by magnetic stirring at 50 °C, until it completely dissolved. The liquid mixtures were slightly yellowish and transparent prior to crosslinking. Following, the mixtures were placed in a vacuum oven for degassing.

Two transparent glass plates covered with Teflon film were utilized for the photopolymerization of the mixtures. In this case, the Teflon film was used to permit an easy removal of the crosslinked polymer structures, because the adhesion between the polymer and the Teflon was quite weaker compared to glass. In brief, the degased mixtures were dropped onto one glass plate and the other plate was slowly lowered down. A gap of approximately 1 mm between the plates was controlled through metal strips insertion between the two glass plates and the mixtures were confined between the plates. The entire setup was subsequently exposed to a shuttered UV floodlight (IntelliRay 400, Uvitrон International, Inc., United States) and the material was cross-linked for 1 h. Following cross-linking, the pure PSN preceramic plates were yellowish and transparent, while the PSN-DVB plates became slightly white and less transparent. To prepare the layered thermistor prototype, a pure PSN film of ~0.8 mm in thickness was firstly cross-linked, and consequently another layer of PSN-DVB of ~0.2 mm in thickness was cross-linked onto the surface of the pure PSN film. The thickness was controlled through the selection of metal strips with corresponding thicknesses to be inserted between the two glass plates.

The cross-linked precursors were subsequently cut into individual samples with a surface area of roughly 20 mm × 100 mm, covered with graphite papers on both sides and placed into an alumina boat for the subsequent pyrolysis. The pyrolysis was conducted under nitrogen flow at 1000 °C for 4 h in a quartz tube furnace (GSL-1100X, MTI KJ GROUP, China), with a heating rate of 1 °C/min.

2.2. Characterization methods

The linear shrinkage of the samples subsequently to pyrolysis was calculated from the change in dimensions and the density was measured in water through the Archimedes’ principle. The thermogravimetric (TG) curves of the cross-linked polymers were recorded over the temperature range from the RT to 1400 °C with a Mettler-Toledo thermogravimetric analyzer (DSC 3+), through the application of a heating rate of 5 °C/min under nitrogen protection.