Aerosol jet printing of nickel oxide nanoparticle ink with ultraviolet radiation curing for thin-film temperature sensors

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Abstract
In this study, the ultraviolet (UV) radiation curing process and furnace curing process for curing aerosol jet printed nickel oxide (NiO) nanoparticle thin films were investigated. NiO has a negative temperature coefficient and can be used to fabricate temperature sensors. Four UV power settings (for 10 min) and four furnace temperatures (for 1 h) were used to cure the aerosol jet printed sensors. The resultant sensor resistance at 100 °C and 180 °C was measured, and the sensor’s sensitivity was characterized by a $B$ value. Confocal microscopy was performed to characterize the sensor surface. The 60% UV power setting yields the lowest resistance and the highest $B$ value among all sensors. The analysis of variations shows that the UV power setting is not a significant factor in the resistance and $B$ value, while the furnace temperature is a significant factor. This indicates that UV curing is a more robust method and does not need to be optimized to achieve good results. The UV curing process not only reduces the required curing time but also improves the performance of the temperature sensor.

Keywords Aerosol jet printing · 3D printing · Thermistor · Curing

1 Introduction
Temperature sensors are used in many research and industrial applications, such as integrated circuit chips [1], micro-resistance temperature detector arrays [2], and measuring metal cutting temperature [3]. Thermistors, made with a material that has a negative temperature coefficient (NTC), are a common type of temperature sensor. The electrical resistance of a NTC thermistor decreases non-linearly when the temperature increases [4]. NTC thermistors are mostly composed of transition metal oxides made of nickel (Ni) and combined with manganese, cobalt, and copper [4–7]. Alternate materials, such as samarium (Sm) and terbium (Tb), for NTC thermistors, are used in order to expand the measurable temperature range have also been reported up to 1000 °C in comparison to the typical maxima temperature up to 500 °C [8]. In addition to the measurable temperature range, sensitivity is another important indicator for the performance of a sensor. The sensitivity of a NTC sensor can be characterized using the B constant [10]. Commercial NTC thermistors usually have a $B$ value above 3500 K [11]. The required facilities to fabricate temperature sensors using conventional processes are expensive and time-consuming. These processes consist of at least four steps including raw precursor molding, pre-sintering precursor, sintering precursor at 1000 °C for several hours, and thermistor packaging [12]. The sintering process is especially time-consuming.

Additive manufacturing (AM) processes such as inkjet printing and screen printing have been applied to fabricate temperature sensors in order to simplify the conventional process [13]. Huang et al. used the inkjet printing process to fabricate temperature sensors using a NiO nanoparticle-based ink [11]. The thermistor can operate over a wide range of temperature from 20 to 250 °C with a great sensitivity (4000 K in $B$ value). This process reduces the number of steps and material waste in comparison to conventional manufacturing processes. Aerosol jet printing (AJP) is a direct writing process and is one of the printing techniques that has been used to fabricate lines under 20 μm with inks and resins [14]. AJP is capable of depositing materials on the curved substrate at room temperature and atmospheric pressure [15] and can work with inks of a wide range of viscosity (1–2500 cP) and multiple types of materials, including polymers and...
metals. The AJP process deposits materials in a continuous line and is different from the inkjet printing process that uses piezoelectric actuators to generate droplets in a discontinuous manner. Therefore, AJP produces both a smooth and fine line as compared to lines printed by inkjet.

The curing process is often required for 3D printing processes that use inks containing metal nanoparticles, such as silver and copper, in order to remove solvents or to sinter particles [16]. Thermal approaches, such as furnace heating, are commonly used for the curing process. The sensitivity of NTC thermistors depends on the curing time and the curing temperature. Wang et al. fabricated a thermistor on a turning insert using AJP and achieved a $B$ value of 4310 K [10]. However, the fabrication process includes a 1-h furnace curing process. The optimal furnace curing temperature has not been determined. A more robust and time-efficient curing method which leads to consistent and high-performance temperature sensors is still needed. Photonic heating approaches including laser and UV heating are two alternative approaches for curing and have the potential to reduce the curing time. Metal nanoparticles show very intense surface plasmon resonance bands in UV to visible regions of the electromagnetic spectrum [17, 18]. The selective heating approach using visible light has been applied to cure or sinter metal nanoparticles with LED light (wavelength is 400 nm) [19] and plasmon resonance [20]. El Kemary et al. [21] investigated the optical absorption spectra of NiO nanoparticles and showed that for NiO nanoparticles, the strongest absorption spectrum is at about 329.5 nm wavelength. Therefore, UV radiation could be an efficient way to sinter NiO nanoparticles. Polzinger et al. applied UV light on silver nanoparticles and found that a lower electrical resistance corresponds to the better consistency of nanoparticles [22]. Saleh et al. [16] 3D-printed electronic circuitry using inks with silver nanoparticles sintered by UV radiation. Wunschler et al. suggested that UV radiation can be used as an assisted sintering approach in conjunction with other thermal treatment techniques for better efficiency [23]. They also pointed out that increasing efficiency and decreasing the costs of the post-curing process are still needed to promote 3D-printed sensors and electronic devices to an industrial scale. UV sintering offers a cost-effective approach and can be integrated with the 3D printing systems which can significantly reduce the fabrication time of multiple layers.

The goal of this study is to develop an optimized UV curing process for the fabrication of thermistors using AJP. Thermistors post-cured by UV will be compared with thermistors cured by furnace heating. The performance of the thermistors will be evaluated, including the consistency of particle curing to be assessed by measuring their electrical resistance and the sensitivity using the $B$ value.

## 2 Method

### 2.1 Ink preparation

For the thermistor, the preparation procedure and the formula of NiO nanoparticle ink for inkjet printing proposed by Huang et al. [11] were modified for AJP which requires an average particle size of 50 nm. The composition of the ink includes 0.5 g of NiO nanoparticles (SkySpring Nanomaterials, Inc., Houston, TX, USA), 2 g of propylene glycol methyl ether (PGME), and 8 g of deionized water. To increase the particle suspension stability, the pH value of NiO nanoparticle ink was adjusted by HNO3 solution and NaOH solution. The suggested pH value for AJP ink is between 3 and 5 in order to avoid particle aggregation [10]. Figure 1 shows examples of NiO nanoparticle inks printed with aggregated and non-aggregated nanoparticles. The ink mixture was then centrifuged at 3000 revolutions per minute for 10 min and filtered with a 0.45-μm syringe filter to remove any remaining large particle aggregates before being used for AJP. For the conducting pad, a silver nanoparticle ink (PV Nano Cell, Migdal Haemek, Israel) was used.

![NiO nanoparticle ink](image1.png)

**Fig. 1** NiO nanoparticle ink printed by AJP: a aggregated particles and b non-aggregated particles. The scale bars represent 100 μm
2.2 Fabrication process

An aerosol jet printer, Optomec AJ-300 (Optomec, Albuquerque, NM, USA), was used in this study to fabricate temperature sensors, as shown in Fig. 2. The nozzle, with a diameter of 150 μm, was positioned 1 to 5 mm above the substrate. The ink was aerosolized with either the pneumatic or ultrasonic atomizer depending on the ink viscosity. The ultrasonic atomizer (Fig. 2b) is for low-viscosity inks (1–10 cP) and the pneumatic atomizer (Fig. 2c) is for high-viscosity inks or resin (10–2500 cP). The silver ink (26 cP) was atomized by the pneumatic atomizer and the NiO ink (1.52 cP) was atomized by the ultrasonic atomizer. To install a thermistor on any shape of the surface, the sensor was printed on a thermal resistant tape, Kapton® (DuPont™, Inc., Wilmington, DE, USA) which is a flexible substrate. Figure 3 illustrates the fabrication process. In step 1, a pair of conductive pads consisting of three layers (7 μm) of silver ink was printed on the thermal resistant tape as electrodes. These were cured by a furnace at 180 °C for 30 min. In step 2, five layers of NiO ink were printed on top of the electrode. In step 4, the printed sensors were cured by either UV radiation (OmniCure S2000 Spot UV Curing System, Excelitas, Waltham, MA USA) using different power settings for 10 min or furnace heating (Neycraft Vulcan 3–550, Dentsply, York, PA, USA) at different temperatures for 1 h.

2.3 Experimental design

To optimize and compare the performance of UV curing and furnace curing, different UV power settings and furnace temperatures were used. These temperature settings are summarized in Table 1. The maximum power output of UV light is 30 W/cm², which can be adjusted by changing the output percentage. For UV curing, the power settings were 60%, 65%, 70%, and 75% with a fixed 10-min curing time. The range of UV power settings was selected based on preliminary studies which showed deformed tape when the power is higher than 75%. For furnace curing, the temperature settings were 200 °C, 240 °C, 260 °C, and 280 °C with a fixed 1-h curing time. The minimal curing temperature of...
200 °C was suggested by Huang et al. [11]. The tape also deformed when exposed to a temperature over 280 °C in the furnace. Therefore, the temperature range was selected to be 200 to 280 °C. For repeatability, there are three sensors were fabricated in each setting.

2.4 Sensor characterization

Figure 4 shows the experimental setup for sensor characterization. The sensors were placed on a heat plate alongside a calibrated reference thermometer (ThermoWorks, American Fork, UT, US). The heat plate was used to raise the temperature to 100 °C (373.15 K) and 180 °C (453.15 K). When the temperature became stable, the resistance of the thermistor was measured using a digital multimeter, HP 34401A 6.5 (HP, Palo Alto, CA, US). Each sensor and temperature setting was tested three times to ensure repeatability. The $B$ value represents the sensitivity of an NTC sensor and was used to characterize all printed temperature sensors. The higher the $B$ constant, the better the sensitivity. The $B$ value (K) can be calculated using the Arrhenius equation (Eq. (1)) [10]

$$B \text{ value} = \frac{\ln(R_1) - \ln(R_2)}{\frac{1}{T_1} - \frac{1}{T_2}}$$

where $R_1$ and $R_2$ represent the resistance measured at temperature $T_1$ (373.15 K) and $T_2$ (453.15 K), respectively. Each sensor was measured at least three times. The printed silver pads help reduce the variation between measurements and mitigate the contact issue between the probe and the sensor. The microstructure of the deposited NiO thin films was examined with confocal microscopy, Keysight VK-X210 (Keyence Corporation, Osaka, Japan) with 20 times and 150 times magnification. A single-factor analysis of variance (ANOVA) was performed using Excel (Microsoft, Redmond, WA, US) to determine the statistical difference ($p$ value < 0.05) between two curing methods [24].

3 Results and discussion

Figure 5a and b show the resistances of sensors cured by UV radiation at 100 °C and 180 °C, respectively. The sensor cured by 60% UV power has the lowest resistances for
both 100 °C and 180 °C. A lower resistance indicates better consistency of sintered particles [22]. The resistance values slightly increase as the UV power increases. Figure 6a and b show the resistances of sensors, measured at 100 °C and 180 °C, respectively, cured by the furnace using different temperatures for 1 h. The sensor cured by 260 °C shows the lowest resistance for both 100 °C and 180 °C.

Figure 7 shows the B values of sensors cured by both UV and furnace. Every sensor has a B value above 4000 K which is higher than 3500 K, the typical requirement for commercial thermistors [11]. The sensors cured by 60% UV power have the highest B value, 5301.65 K, among all sensors. The highest B value among sensors cured by the furnace is 5231.68 K from sensors cured at 260 °C. The average B value for all UV power settings and furnace temperatures is 5079.19 K and 4618.6 K, respectively. The ANOVA shows that there is a significant difference in B value between the two curing methods (p-value < 0.05). Also, there is no significant difference in B value among different UV power settings while there the difference in B value is significant among different furnace curing temperature. This indicates that UV curing is a more robust curing process than furnace curing, as the B value, a performance measure of temperature sensors, is less sensitive to the UV power setting. When using furnace curing, the temperature needs to be optimized to achieve the best sensitivity. The B values achieved in this study are all higher than 4310 K, the B value reported by a previous study that used AJP to fabricate temperature sensors [10]. This shows an improvement of the sensor’s sensitivity by optimizing the curing process. Moreover, the UV curing process only takes 10 min. In comparison to the 1-h furnace curing time, the total fabrication time can be reduced significantly.

Figure 8a–d show the confocal microscopy images (150x) of surfaces from sensors with the highest (60% and 260 °C) and lowest B values (75% and 280 °C) for both curing methods. In Fig. 8a and c, NiO nanoparticles closely form a consistently thin film, and these two sensors correspond to the lowest resistance and the highest B value, cured by 60% UV and 260 °C, respectively. Figure 8b shows
the sensor surface cured by 75% of UV power. There are a few visible cracks, indicated by arrows. The cracks can contribute to the increase in resistance and inconsistency. In Fig. 8d, some aggregated particles can be observed. However, even with the existence of those minor defects, the sensors still exhibit good sensitivity. Figure 8e–h show the color maps of height variations on the sensor surfaces. In all color maps, several NiO particles on the surface are clearly visible as high spots. Figure 8g shows the most even surface and Fig. 8f shows the most variation in heights. Table 2 summarizes the resistances (at 100 °C and 180 °C), B values, and surface roughness (Ra) of the sensors shown in Fig. 8. The sensor cured by a furnace at 260 °C has the lowest Ra. Sensors cured by 60% UV power and 260 °C have lower Ra than those cured by 75% UV power and 280 °C. A lower Ra, indicating a smoother surface, can lead to a lower resistance and better consistency. Although furnace curing shows a lower overall Ra value, owing to a gentle curing process, the curing time is much longer than UV curing. There are some limitations in Ra measurement. The silver paths are under the thin NiO film and the deformation of the substrate can cause variations on the surface. Therefore, instead of covering the whole sensor area for Ra measurement, areas between silver lines were chosen for Ra measurement to minimize the effect of substrate deformation.

Figures 9 and 10 show the confocal microscopy images of a corner of the sensors cured by UV and furnace, respectively. In Fig. 9a and Fig. 10a, the black areas are the printed NiO sensor and the grey strips are the silver conductive lines. Figure 9b and Fig. 10b show the color height map of Fig. 9a and Fig. 10a, respectively, in which red corresponds to the high and blue corresponds to the low points. The profile of the sensor and silver path can be observed easily. Figure 11 shows the extracted height profiles along with the numbered areas in Fig. 9a and Fig. 10a. The average heights in the numbered areas are labeled in Fig. 11. The thickness of the sensor can be estimated by subtracting the height of the substrate from the height of the NiO thin-film area. For example, as shown in Fig. 11b, the height in (4) is 116.73 μm (substrate) and the height in (6) is 121.47 μm (NiO thin film), leaving a difference of 4.74 μm which is the thickness of the thin film. However, in the case of Fig. 11a, the substrate is not flat, due to the deformation of the heat resistant tape, and thus, it is difficult to measure the thickness of the NiO thin film. This can also be observed in Fig. 9b which shows a higher top right corner and a lower bottom left corner in the thin

| Curing method       | Resistance at 100 °C (MΩ) | Resistance at 180 °C (MΩ) | B value       | Roughness (Ra) |
|---------------------|---------------------------|---------------------------|---------------|----------------|
| UV radiation (60%)  | 88.8                      | 7.23                      | 5301.7 K      | 1.87 μm        |
| UV radiation (75%)  | 107.5                     | 9.5                       | 5007.5 K      | 2.44 μm        |
| Furnace (260 °C)    | 106.8                     | 8.83                      | 5231.7 K      | 1.63 μm        |
| Furnace (280 °C)    | 118.5                     | 13.8                      | 4536.2 K      | 2.15 μm        |
film. This observation indicates that furnace curing is a gentler curing process which leads to less deformation of the substrate, although the process takes a longer time. A closer examination of the substrate deformation when using UV curing can be conducted further in the future.

4 Conclusions

This study explores an efficient UV radiation curing method for AJP of NiO nanoparticles ink for the fabrication of thin-film temperature sensors. The UV curing
process significantly reduces the curing time from 1 h to 10 min making the fabrication process much more efficient. The 60% UV power setting shows the best results among all sensors. 260 °C furnace shows the best results among the four furnace curing temperatures. On average, the UV-cured sensors also show significantly higher B values, an indicator of the sensor’s sensitivity, than those that underwent furnace curing. While the furnace curing temperature has a significant effect on the B value, the UV power setting does not have a significant effect. This indicates that UV curing is a more robust method for curing and does not need to be optimized as much as the temperature for furnace curing. The confocal microscopy results show that over curing may cause micro-cracks on the sensor surface, thus reducing the consistency and sensitivity. Future work can include using even lower radiation output to minimize the deformation of the substrate or a higher radiation output with a shorter curing time.

Author contribution Yi-Tse Chang: conception, analysis, execute experiments, writing—original draft preparation and editing, visualization—original draft preparation. Kuan-Yi Hung: conception and analysis, Hong-Tsu Young: writing—review and editing, supervision. Kuan-Ming Li: writing—review and editing, supervision. Roland K. Chen: visualization—review and editing, writing—review and editing, supervision.

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Availability of data and material The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code availability Not applicable.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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