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Heat generation characteristics of microheaters prepared with ITO nanoparticles and organic additives

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ABSTRACT

In this study, we demonstrate the heat generation characteristics of microheaters prepared with an ITO nanoparticle (NP) paste, which is a mixture of ITO NPs, polymethyl methacrylate, and terpineol. A comparison with microheaters prepared with ITO NPs only shows that the organic additives substantially enhance their heat generation characteristics. The maximal temperature obtained is 445 °C at a bias voltage of 12 V, which is three times higher than for the NP microheaters. Moreover, the NP-paste microheaters have better thermal stability and a more uniform heating zone. The enhancement in the heat generation characteristics results from the smoother surfaces and the higher density of the NP-paste films.

1. Introduction

Recently, microheaters made of nanomaterials have gained popularity in the field of microsensors since solution-processable nanomaterials facilitate the fabrication of low-cost sensors through simple production routes [1–6]. Especially, microheaters are one of the important components of micro gas sensors in which they determine the responsivity and sensitivity of these sensors because high temperatures are required for the effective operation. Microheaters can attain high temperatures due to joule heating, when sufficient voltages are applied across them. Among the nanomaterials used to make microheaters, ITO nanoparticles (NPs) are one of the most suitable for high-temperature microheaters because they are more resistant to oxidation than carbon nanotubes (CNTs) and graphene. Nevertheless, few studies have been reported on ITO NP pastes to fabricate high-efficiency microheaters.

A significant amount of research has been performed, however, on electrode films made of metal NP pastes consisting of metal NPs and organic additives, for applications as dispersants and binders [7–11]. According to previous studies, choosing an appropriate binder is essential for metal NP pastes, so that electrode films are formed without the exfoliations that degrade their electrical properties. Exfoliation is a problem for solution-processed thin films and its elimination is the first step to achieving high-quality films. The dispersant also plays an important role in solution-processable technologies using nanomaterials. It prevents the aggregation of nanomaterials and facilitates their uniform dispersion in solvents. Based on the researches on metal NP pastes, we aim to prepare the ITO NP-paste suitable for a microheater. We, therefore, employ organic materials in this study as dispersant and binder to prepare ITO NP pastes, and we investigate the effect of the organic additives on the heat generation characteristics of ITO NP-paste microheaters by comparing their properties with those of microheaters made of ITO NPs only. Table 1 shows the materials used in this study. Polymethyl methacrylate (PMMA) is used to disperse ITO NPs homogeneously in the paste and α-terpineol facilitates binding between ITO NPs and the quartz substrates during sintering.

2. Experimental procedure

The fabrication steps and schematic structure of our ITO NP-paste microheater are described in Fig. 1(a) and (b), respectively. All of the materials used in this study were purchased from Sigma–Aldrich except the ITO NPs purchased from LTS research laboratories Inc. First, ITO NPs with an average size of 45 nm were dissolved in ethanol at 30 wt% concentration, and PMMA powders were dissolved in chloroform at 5 wt% concentration. The PMMA solution mixed with terpineol at a weight ratio of 7:3 was sonicated for 5 min. The PMMA-terpineol and the NP solutions were mixed at a weight ratio of 2:8 before being sonicated for 5 min to give the NP paste. In order to fabricate a microheater, the NP paste was spin-coated on a quartz substrate with 1 mm × 1 mm patterns, and then

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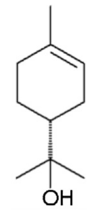
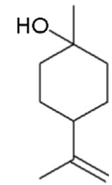
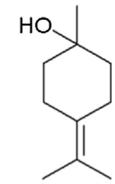
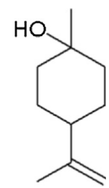
Table 1
Details of the chemicals (solvent, binder, and dispersant) and the ITO NPs used in this study.

Chemical and NPs	Role and properties	Structure
Chloroform	Solvent, bp = 61.2 °C	$CHCl_3$
α-Terpineol	Binder, bp = 219 °C Viscosity = 36.5 cp	 ~65 %  ~10 %  ~20 %
Polymethyl methacrylate	Dispersant, M_w = 97,000	 ~10 %
ITO NP solution		
Ethanol	Solvent, bp = 78.4 °C	CH_3CH_2OH
ITO NPs	Heat generation material	Cubic, a = 10.22 Å, d = 45 nm

dried at 100 °C for 3 min in air. The spin-coating and drying processes were repeated 10 times and the films were sintered at 800 °C for 15 s, and then at 400 °C for 10 min, in vacuum. For comparison, an NP microheater made of ITO NPs only was fabricated following the same procedure with an equivalent concentration of ITO NPs. After sintering, silver solder paste was painted on both ends of the films to form the electrodes. The electrical properties were measured using a semiconductor parameter analyzer (Agilent 4155C) and the temperatures of the microheaters were measured using an infrared (IR) camera (FLIR-A645SC) with a 2% uncertainty and a sensitivity of 30 mK in air. The structural properties of the films were analyzed by X-ray diffraction (XRD; Philips, Xpert system) and imaged using a field emission scanning electron microscope (FE-SEM; Hitachi, S-4300).

3. Results and discussion

Fig. 2(a)–(c) shows the ITO XRD reference (JCPDS card #88-0773), and XRD patterns of ITO NP films without and with the organic additives, respectively. No difference is visible between the basic elements of the XRD patterns of the two NP-based films. However, a slight difference in the linewidth of the XRD peaks can be seen, indicating different grain sizes. Using the Scherrer equation [12], the average grain sizes are calculated to be 21 and 15 nm for the NP and NP-paste films, respectively. The grain size is reduced compared with the precursor ITO NPs, and the average grain size in the NP-paste film is smaller than in the NP film. The reduction in grain size is attributed to the sonication carried out before spin-coating [13–16]. Sonication is a well-established method to reduce the size of inorganic micrometer- and nanometer-scale particles [17,18]. As for the smaller grain size in the NP-paste film, this is related to the effect of the PMMA dispersant during sonication. The carbonyl groups present in PMMA chelate ligands attached to a central metal ion. PMMA is thereby coated on the surface of the NPs, which retards NP agglomeration in the NP-paste solution.

The effects of the organic additives on the heat generation characteristics of the NP-based microheaters are demonstrated in Fig. 3. Fig. 3(a) shows the I–V characteristics of the ITO NP film and the ITO NP-paste film, demonstrating that the magnitude of the current of the ITO NP-paste film is nearly five times greater than that of the ITO NP film. In addition, the sheet resistances of the ITO NP-paste film and ITO NP film are 23.5 and 280 Ω/sq, respectively. The electrical characteristics of the films directly affect the amount of heat generated from the microheater since there is a proportional relationship between the heat and the current. In terms of the heat generated as a function of the bias voltage, as shown in Fig. 3(b), the temperatures obtained with the NP-paste microheater are higher than those generated by the NP microheater, indicating that the former is more efficient. Fig. 3(b) shows the steady-state temperatures of the microheaters. The NP-paste microheater can generate temperatures above 200 °C, which is the minimum temperature for microsensor applications. The highest temperatures obtained are respectively 445 °C and 130 °C for the NP-paste and the NP microheaters, at a bias voltage of 12 V. Fig. 3(c) shows the temperatures recorded over 120 s for the NP and the NP-paste microheaters at a bias voltage of 9 V, indicating that both generate heat in a stable manner. In this study, we chose a bias voltage of 9 V to investigate the thermal stability as a function of time for the NP and the NP-paste microheaters because the temperature obtained at the bias voltage for the NP-paste microheater is appropriate for plastic-based gas sensors in which its temperature should be lower than 300 °C, the maximum endurable temperature of a plastic substrate. For the NP-paste microheater in particular, the thermal stability at temperatures above 200 °C is remarkable compared with films made of other

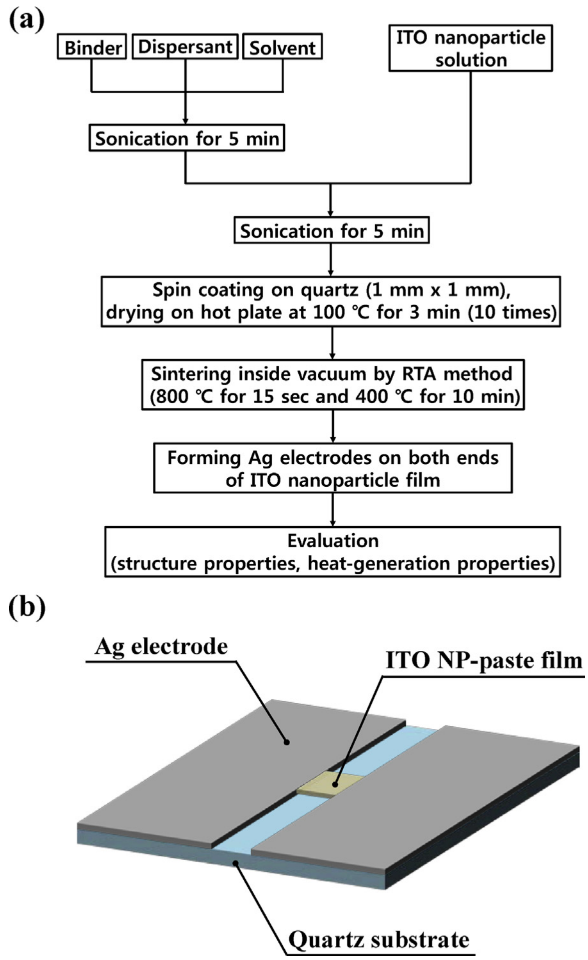


Fig. 1. (a) Flow chart of the experimental procedures used to fabricate an ITO NP-paste microheater. (b) The schematic structure of the ITO NP-paste microheater.

nanomaterials [19–23]. The superior heat generation characteristics of the NP-paste microheater are related to the organic additives present in the NP paste.

Fig. 4 shows top-view and cross-sectional FE-SEM images of the NP and NP-paste films. Comparing the top-view images in Fig. 4(a) and (b), the surface of the NP film is rough with larger clusters, while the NP-paste film has a smoother surface morphology, a consequence of the dispersant effect of PMMA. As mentioned above, PMMA promotes the homogeneous dispersion of ITO NPs in

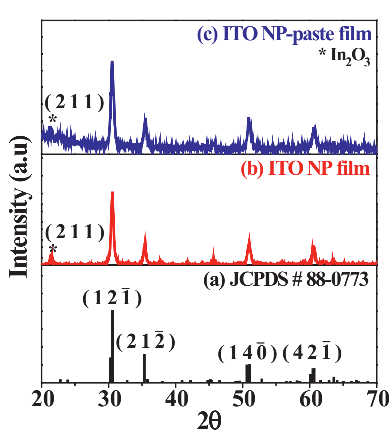


Fig. 2. X-ray diffraction patterns of (a) JCPDS card #88-0773, (b) the ITO NP film, and (c) the ITO NP-paste film.

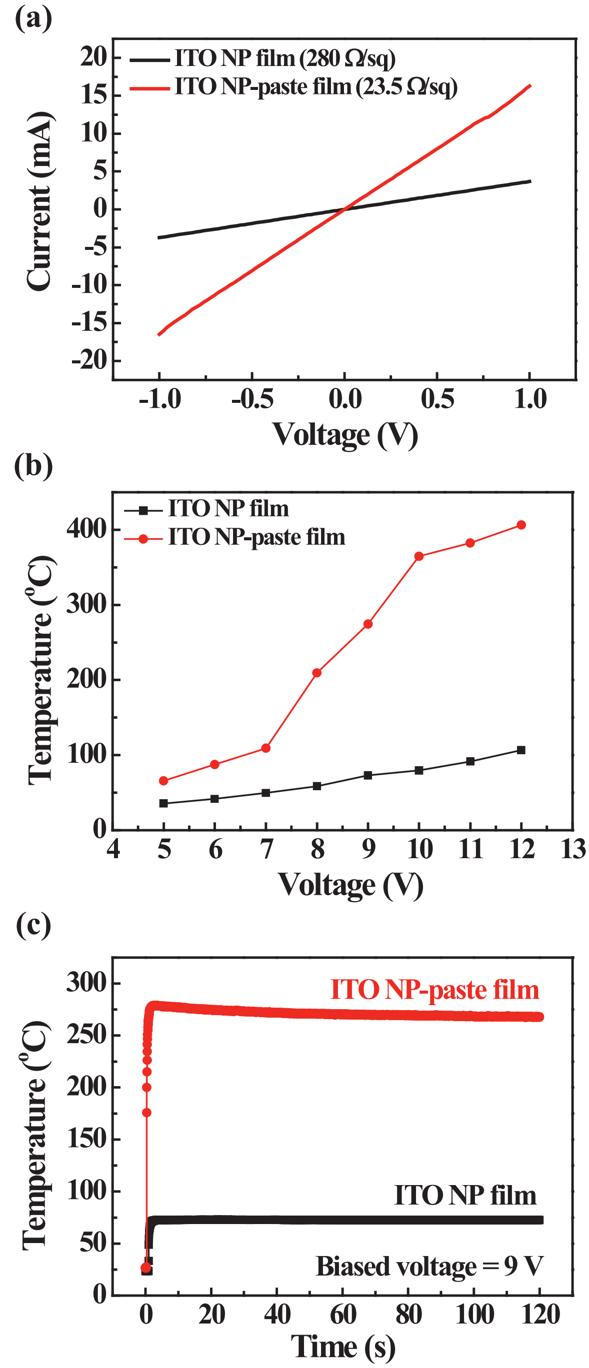


Fig. 3. (a) The *I–V* characteristics of the NP and the NP-paste films. (b) Temperature of the NP and the NP-paste microheaters as a function of the bias voltage. (c) Temperature as a function of time for the NP and the NP-paste microheaters at a bias voltage of 9 V, emphasizing their thermal stability.

solution and as a result, a more uniform film is formed with a smoother surface. A rough surface induces electron surface scattering and increases the resistivity of the film [24,25]. In that regard, the NP-paste film with a smooth surface should have superior electrical properties to the NP film with a rough surface. On the other hand, the effect of the terpineol binder can be seen in the cross-sectional images of Fig. 4(c) and (d). Exfoliation is observed in the NP film but not in the NP-paste film, and this is attributed to terpineol facilitating the adhesion of the NPs to the quartz substrate during sintering. Furthermore, the binder helps

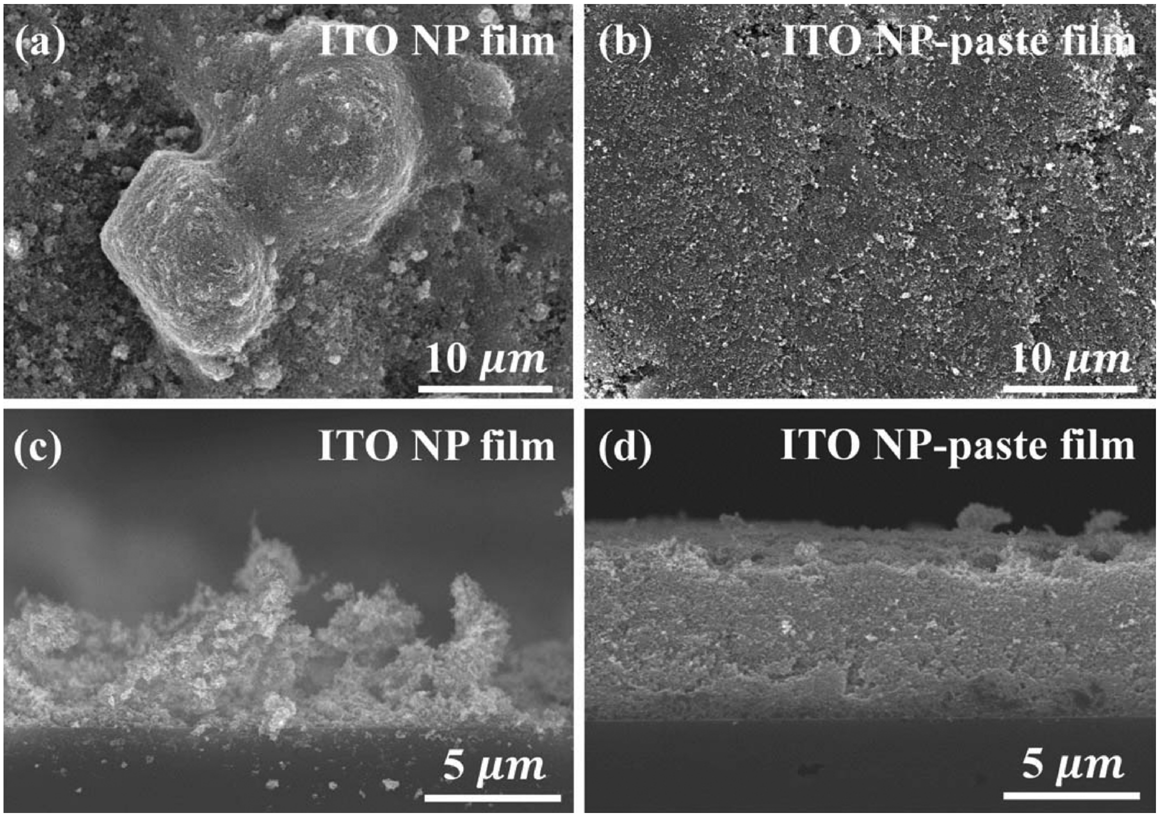


Fig. 4. (a, b) Top-view and (c, d) cross-sectional FE-SEM micrographs of (a, c) the NP and (b, d) the NP-paste films.

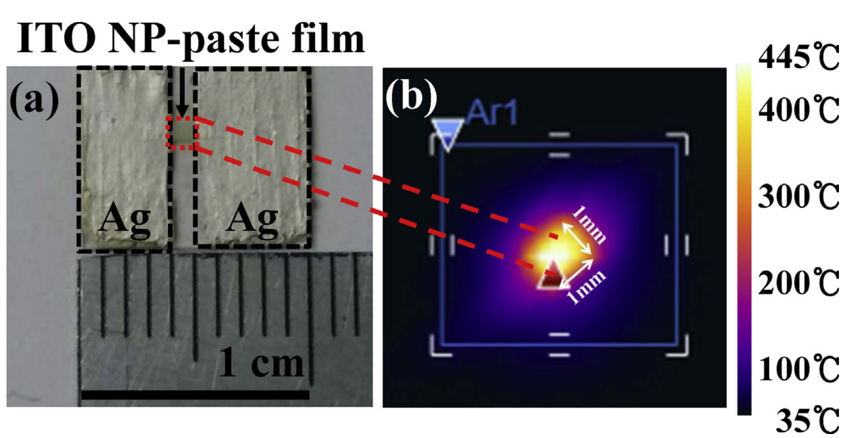


Fig. 5. (a) Optical and (b) IR images of the NP-paste microheater. The IR image was taken at a bias voltage of 12 V.

increase the NP density, which in turn is responsible for the excellent heat generation characteristics of the NP-paste microheater. Consequently, the NP-paste microheater that has strong attachments between the NPs and the substrate as well as between the NPs owing to the organic additives is superior to the microheater made of the NP only in heat generation characteristics.

The optical and the IR images of the NP-paste microheater under an applied voltage of 12 V are shown in Fig. 5(a) and (b), respectively, where the location of the 1 mm^2 NP-paste film is indicated with dashed lines. The IR image shows that a uniform temperature zone at 445 °C is formed in the region of the NP-paste film. Considering that microheaters are required to generate temperatures above 200 °C uniformly, the NP-paste microheater proposed in this study is a promising candidate for the next generation of high-efficiency microheater.

4. Conclusions

In this study, we have developed a microheater prepared with an NP-paste consisting of ITO NPs, PMMA dispersant, and terpineol binder. The effects of the organic additives on the heat generation characteristics of NP-paste microheaters were investigated in comparison with those of microheaters made of ITO NPs only. The NP-paste microheater generates temperatures above 200 °C in a stable manner and its high performance stems from the effects of the organic additives during the formation of NP-paste films. Because of the PMMA dispersant and the terpineol binder, the

NP-paste films have relatively smoother surfaces and densify during sintering. The latter avoids exfoliation in the resulting films and explains the excellent heat-generation characteristics of our proposed microheater.

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References

[1] Y.H. Yoon, J.W. Song, D. Kim, J. Kim, J.K. Park, S.K. Oh, C.S. Han, Adv. Mater. 19 (23) (2007) 4284–4287.
[2] D. Sui, Y. Huang, L. Huang, J. Liang, Y. Ma, Y. Chen, Small 7 (22) (2011) 3186–3192.
[3] J. Kang, H. Kim, K.S. Kim, S.K. Lee, S. Bae, J.H. Ahn, Y.J. Kim, J.B. Choi, B.H. Hong, Nano Lett. 11 (12) (2011) 5154–5158.
[4] K. Im, K. Cho, J. Kim, S. Kim, Thin Solid Films 518 (14) (2011) 3960–3963.
[5] T. Markevicius, R. Furferi, N. Olsson, H. Meyer, L. Governi, M. Carfagni, Y. Volpe, R. Hegelbach, Nanomater. Nanotechnol. 4 (8) (2014) 1–13.
[6] K. Im, K. Cho, K. Kwak, J. Kim, S. Kim, J. Nanosci. Nanotechnol. 13 (5) (2013) 3519–3521.
[7] J.G. Bai, Z.Z. Zhang, J.N. Calata, G.Q. Lu, IEEE Trans. Compon. Packag. Manuf. Technol. 29 (3) (2006) 589–593.
[8] T. Wang, X. Chen, G. Lu, G.Y. Lei, J. Electron. Mater. 36 (10) (2007) 1333–1340.
[9] J. Yan, G. Zou, A. Wu, J. Ren, J. Yan, A. Hu, Y. Zhou, Scr. Mater. 66 (8) (2012) 582–585.
[10] H.G. Kim, J. Park, G.H. Lee, Mater. Chem. Phys. 140 (1) (2013) 419–426.
[11] L. Yun, A. Pearl, M.J. Christopher, L. Shuguang, Proceedings of CIPS 2014, Nuremberg, February, 1–7, 2014.
[12] A. Weibel, R. Bouchet, F. Boulc'h, P. Knauth, Chem. Mat. 17 (9) (2005) 2378–2385.
[13] A.E. Kandjani, M.F. Tabriz, B. Pourabbas, Mater. Res. Bull. 43 (2008) 645–654.
[14] E.E. Gharedaghi, M.A. Faramarzi, M.A. Amini, A.R. Najafabadi, S.M. Rezayat, A. Amani, Pharm. Dev. Technol. 17 (5) (2012) 638–647.
[15] F. Franco, L.A. Perez-Maqueda, J.L. Perez-Rodriguez, J. Colloid Interface Sci. 274 (2004) 107–117.
[16] F. Franco, J.A. Cecila, L.A. Perez-Maqueda, J.L. Perez-Rodriguez, Appl. Clay Sci. 35 (1) (2007) 119–127.
[17] J. Jiang, G. Oberdorster, P. Biswas, J. Nanopart. Res. 11 (1) (2009) 77–89.
[18] M.X. Reinholdt, F. Hubert, M. Faurel, E. Tetre, A. Razafitianamaharavo, F. Francius, D. Pret, S. Petit, E. Bere, M. Pelletier, E. Ferrage, Appl. Clay Sci. 77 (2013) 18–32.
[19] P. Liu, L. Liu, K. Jiang, S. Fan, Small 7 (6) (2011) 732–736.
[20] S. Sorel, D. Bellet, J.N. Coleman, ACS Nano (2014) , doi:http://dx.doi.org/10.1021/nn500692d.
[21] D. Kim, L. Zhu, D.J. Jeong, K. Chun, Y.Y. Bang, S.R. Kim, J.H. Kim, S.K. Oh, Carbon 63 (2013) 530–536.
[22] D. Jung, D. Kim, K.H. Lee, L.J. Overzet, G.S. Lee, Sens. Actuators A Phys. 199 (2013) 176–180.
[23] H.S. Jang, S.K. Jeon, S.H. Nahm, Carbon 49 (2011) 111–116.
[24] H. Marom, M. Eizenberg, J. Appl. Phys. 99 (2006) 123705–123705-7.
[25] Y. Ke, F. Zahid, V. Timoshevskii, K.D. Xia Gall, H. Guo, Phys. Rev. B 79 (2009) 155406–155406-6.