# Highly Flexible Transparent Film Heaters Based on Metallic Nanowires

J-P Simonato*, C. Mayousse*, C. Celle*, A. Carella*

*CEA Grenoble / LITEN / DTNM / LCRE, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France
jean-pierre.simonato@cea.fr

## ABSTRACT

We present the fabrication and characterization of transparent thin film heaters (TTFHs) based on silver nanowires. The goal is to develop a simple process for the production of transparent heating elements by large area printing techniques. The TTFHs are based on recently developed random networks of silver nanowires. Thanks to the very low sheet resistance achievable with silver nanowires, we show that it is possible to obtain high heating rates and good steady state temperatures at low voltages, typically below 12 V.

We will show that TFHs can also be fabricated on highly flexible plastic substrates, with excellent heating performances.

***Keywords***: silver nanowires, random network, transparent, film heater, conductor

## 1 INTRODUCTION

Transparent thin film heaters (TTFHs) represent a considerable market for various applications. Defrosting / defogging of car and plane windows is probably the most well known use of TTFHs. Interestingly, defrosting of windows in airplanes was the first application for TTFHs, permitting high-altitude bombing during World War II.[1] Another typical example is for maintaining LCD displays at optimum operating temperatures for screen response, notably for outdoor LCD displays. Up to now transparent conductive oxides (TCOs) have been widely used for this application, notably zinc oxide derivatives and indium tin oxide (ITO). The properties of TCOs are suitable for most application up to now. However many optoelectronic devices are now evolving to flexible substrates. Many functional systems based on bendable substrates have already been described, including thin film solar cells, OLED or LCD displays, touch screens… For all these devices TCOs can not be considered anymore since they are brittle and thus not resistant to mechanical constraints. Furthermore the manufacturing cost is relatively high, and processes based on indium tin oxide (ITO) are somehow risky because the price of indium is particularly fluctuating due to its scarcity, its increasing use and the still insufficient recycling process.

Several innovative approaches to obtain flexible TTFHs have been developed these last years, in particular with carbon nanotubes [2-7] and graphene [8, 9]. Nevertheless the sheet resistivity of the networks made with these materials at high transparency is still too high for low voltage applications.

At the same time, new transparent conductors have been realized thanks to metallic nanowires. In particular silver nanowires (Ag NWs) are rather easy to make in large amount from batch solution reactions.[10-14] Performances of Ag NWs for conducting electrons at high transparency are excellent with very low sheet resistances, comparable to those of ITO (< 30 ohm.sq$^{-1}$).[14-19] We present herein results on new electrothermal film heaters based on random networks of silver nanowires and we demonstrate that excellent heating performances can be obtained at high transparency, on both rigid and flexible substrates.

## 2 RESULTS AND DISCUSSION

The study was mainly divided into three steps. The nanowires were first synthesized in solution and characterized, then random networks of Ag NWs were prepared on different substrates and finally heating performances were monitored at various applied voltages.

### 2.1 Silver nanowire synthesis

The silver nanowires were synthesized by the polyol method[13] and purified to remove remaining nanoparticles (see Figure 1). The mean length of nanowires was ~8 µm and diameters in the 50-80 nm range. It is important to obtain high aspect ratio nanowires because it allows to fabricate percolating random networks of nanowires with very good ratio between transparency and electrical conductivity. Before the deposition step, Ag NWs were dispersed either in water or organic solvents like alcohols, for instance isopropanol. The solutions of silver nanowires were stable for weeks.

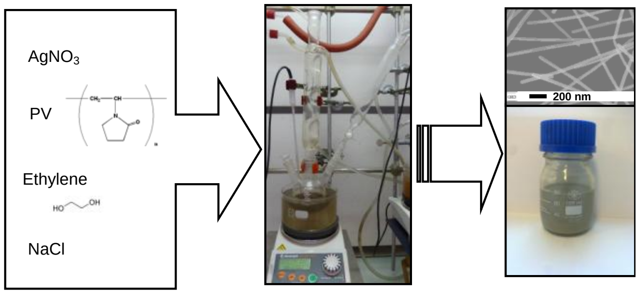


**Figure 1.** Batch synthesis of nanowires from silver salt

## 2.2 Fabrication of random networks of silver nanowires

Various techniques can be used to fabricate transparent electrodes including spin-coating, airbrush spray, drop casting and others.

Glass was used for these first experiments and flexible substrates were also used without any problem in a second time.

Indeed, It is already known that random networks of nanowires can be transferred by PDMS stamps, laminated or embedded in polymers to afford conductive transparent materials with lower roughness.[17 20, 21] Typically, sheet resistances of few tens ohm.sq$^{-1}$ are obtained at 90% transparency in the visible spectrum, down to less than 1 ohm.sq$^{-1}$ at ~60% transmission. These performances are in the same range of those obtained with ITO.

In this study, TTFHs were obtained by spincoating solutions of Ag NWs onto Eagle XG glass substrates obtained from Corning. The sheet resistances of the electrodes were measured by a Loresta-EG four probe resistivity meter and the transmittance in the visible spectrum by a Varian Cary 5000 UV-vis-NIR spectrophotometer.

The power dissipated in a resistive conductor can be described by the Equation $P=V^2/R$, where V is the applied voltage and R the total resistance, thus it can be understood that with low sheet resistance high heat dissipation can be obtained at fixed bias. And precisely, this is a specific advantage of metallic nanowires networks to afford very low sheet resistances at high transparency.


**Figure 2.** TTFHs deposited on glass and placed upon the printed CEA logo.

## 2.3 Heating performances

We prepared the TTFHs by applying silver paste to make a low-resistance contact on two opposite sides of the film. We built an experimental setup for monitoring the temperature increase while DC voltage is applied (Figure 3).

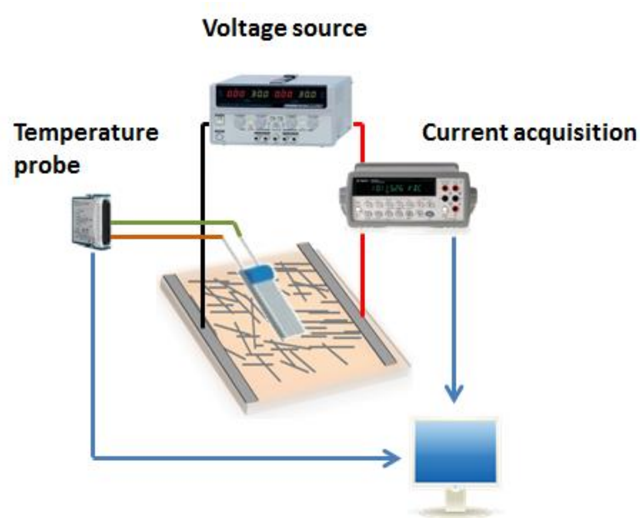


**Figure 3.** Experimental setup for monitoring heat generation of TTFHs at various voltages.

We applied incremental input voltages ranging from 3 to 12V by a DC power supply (Agilent 34410A). We measured the electrical current through the TTFHs and we monitored the heating effect with a thermocouple. Figure 4 shows the temperature plot as a function of time, for a 88% transparent TTFH having a sheet resistance of 80 ohm.sq$^{-1}$.

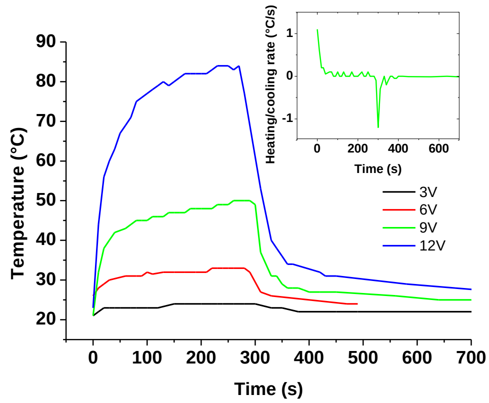


**Figure 4.** Temperature as a function of time for a 80 ohm.sq$^{-1}$ TFH on glass at different applied voltages. Insert: derivative of the temperature vs time at 9V applied voltage.

Steady-state temperatures were significantly different and correlated with applied biases. This is due to the generation of heat by the passage of electricity through a resistance, *i.e.* Joule effect, which is proportional to the square of the applied voltage: $P=V^2/R$. This fits well with observed steady state temperatures, even by taken into account that resistance is slightly modified by increasing the temperature. As shown in the insert, the heating/cooling rates calculated from the derivative of the temperature with respect to time $(\partial T / \partial t)$ was slightly above 1 °C.s$^{-1}$ at an applied voltage of 9V. This is interesting for many applications requiring high heating rates at low voltage.

These results compare very well with other TTFHs based on carbon nanotubes or graphene. Thanks to the low sheet resistance achievable with random networks of silver nanowires, it is possible to reach high temperatures at low voltage, typically below 12 V, which might be for instance of interest for electrical defrosting in automobile systems.

Concerning the mechanical stability of the TTFHs, we did not observe delaminating between the film and substrate even after 10 heating-cooling cycles. However, the film has poor adhesion onto glass and further experiments are in progress to improve bond between the two materials.

We also carried out some experiments onto flexible substrates such as PEN 125 µm thick, and similar results were obtained. Hundreds of bendings of the electrodes at low radius of curvature (5 mm) did not lead to alteration of performances. All the results onto flexible substrates will be presented during the oral communication.

# 3 CONCLUSION

In summary, we developed a new method to fabricate high performance TTFHs based on random networks of Ag NWs. We have shown that it is possible to fabricate film heaters that may be very efficient even at low voltages. This is mainly ascribed to the excellent electrical properties of transparent conductors made with random networks of Ag NWs. We think these results could be a useful approach for the engineering of TTFHs both on rigid and flexible substrates.

# REFERENCES


[1] R. G. Gordon, *MRS Bulletin*, pp. 52-57, 2000.

[2] Y. H. Yoon, J. W. Song, D. Kim, J. Kim, J. K. Park, S. K. Oh, and C. S. Han, *Advanced Materials*, vol. 19, pp. 4284-4287, 2007.

[3] D. Kim, H.-C. Lee, J. Y. Woo, and C.-S. Han, *The Journal of Physical Chemistry C*, vol. 114, pp. 5817-5821, 2010.

[4] H.-S. Jang, S. K. Jeon, and S. H. Nahm, *Carbon*, vol. 49, pp. 111-116, 2011.

[5] Z. P. Wu and J. N. Wang, *Physica E: Low-dimensional Systems and Nanostructures*, vol. 42, pp. 77-81, 2009.

[6] T. J. Kang, T. Kim, S. M. Seo, Y. J. Park, and Y. H. Kim, *Carbon*, vol. 49, pp. 1087-1093, 2011.

[7] E. J. Spadafora, K. Saint-Aubin, C. Celle, R. Demadrille, B. Grévin, J.-P. Simonato, *Carbon*, 10.1016/j.carbon.2012.03.010, 2012.

[8] J. Kang, H. Kim, K. S. Kim, S.-K. Lee, S. Bae, J.-H. Ahn, Y.-J. Kim, J.-B. Choi, and B. H. Hong, *Nano Letters*, vol. 11, pp. 5154-5158, 2011.

[9] D. Sui, Y. Huang, L. Huang, J. Liang, Y. Ma, and Y. Chen, *Small*, vol. 7, pp. 3186-3192, 2011.

[10] Y. Sun, B. Gates, B. Mayers, and Y. Xia, *Nano Letters*, vol. 2, pp. 165-168, 2002.

[11] L. Hu, H. S. Kim, J.-Y. Lee, P. Peumans, and Y. Cui, *ACS Nano*, vol. 4, pp. 2955-2963, 2010.

[12] A. Madaria, A. Kumar, F. Ishikawa, and C. Zhou, *Nano Research*, vol. 3, pp. 564-573, 2010.

[13] S. Coskun, B. Aksoy, and H. E. Unalan, *Crystal Growth & Design*, vol. 11, pp. 4963-4969, 2011.

[14] D.-S. Leem, A. Edwards, M. Faist, J. Nelson, D. D. C. Bradley, and J. C. de Mello, *Advanced Materials*, vol. 23, pp. 4371-4375, 2011.

[15] X.-Y. Zeng, Q.-K. Zhang, R.-M. Yu, and C.-Z. Lu, *Advanced Materials*, vol. 22, pp. 54484-4488, 2010.

[16] L. B. Hu, H. Wu, and Y. Cui, *MRS Bulletin*, vol. 36, pp. 760-765, Oct 2011.

[17] A. R. Madaria, A. Kumar, and C. W. Zhou, *Nanotechnology,* vol. 22, p. 7, May 2011.
[18] V. Scardaci, R. Coull, P. E. Lyons, D. Rickard, and J. N. Coleman, *Small,* vol. 7, pp. 2621-2628, 2011.
[19] Z. Yu, Q. Zhang, L. Li, Q. Chen, X. Niu, J. Liu, and Q. Pei, *Advanced Materials,* vol. 23, pp. 664-668, 2011.
[20] Z. Yu, L. Li, Q. Zhang, W. Hu, and Q. Pei, *Advanced Materials,* vol. 23, pp. 4453-4457, 2011.
[21] W. Gaynor, G. F. Burkhard, M. D. McGehee, and P. Peumans, *Advanced Materials,* vol. 23, pp. 2905-2910, 2011.