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Humidity sensing properties of screen-printed carbon-black and Fe(II) spin crossover compound hybrid films

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Abstract

We report on the humidity sensing properties of a screen-printed polymeric film loaded with carbon-black and $Fe[(Htrz)_2(trz)]BF_4$ nanoparticles. The new film shows excellent humidity sensitivity in a wide relative humidity range and the processing conditions make it suitable for a new generation of inexpensive, resistive humidity sensors on flexible substrates/ tags

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Keywords:

1. Introduction

Nowadays, significant developments in MEMS technology are being introduced, especially those in polymer based-MEMS, which are particularly attractive for their low cost, good processability, bio-compatibility and suitability for use in flexible substrates [1]. The main techniques for the processing of organic MEMS are moulding or photolithography of photosensitive polymers. Among alternative technologies, screen-printing is a well-known low cost technology mainly used in microelectronics for interconnections and packaging purposes. It has been extended to development of polymer based MEMS [2-3]. In particular, carbon-black filled polymers have been used to develop sensitive and inexpensive gas sensors. The individual sensor elements are constructed from films consisting of carbon black particles dispersed into insulating organic polymers. The carbon black endows electrical

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conductivity to the films, whereas the different organic polymers are the source of chemical diversity between sensor elements. Swelling of the polymer upon exposure to a gas/vapour increases the resistance of the film, thereby providing an extraordinarily simple means for monitoring the presence of a gas/vapour [4, 5]. Here, screen-printed hybrid films consisting of carbon-black and a Fe(II) spin crossover compound dispersed in a polymer are studied for humidity sensing. $Fe[(Htrz)_2(trz)]BF_4$, has been of special interest in the scientific community over the last few decades due to its unique spin transition properties near room temperature. This complex has moreover affinity toward humidity in relation with its chemical structure ; this propriety which will be used in our application.

2. Sensor fabrication

The nanoparticles of $[Fe(Htrz)_2trz]BF_4.H_2O$ SCO complex (with Htrz = 1,2,4-1*H*-triazole and trz = the deprotonated triazolato (-) ligand) are prepared by a reverse micelle method [6-7]. The particles are extracted by washing with diethyl ether and a pink powder is collected and characterized by reflectivity and Transmission Electron Microscopy (TEM). The diameter of theses nanoparticles is on average to 45nm.
Sensors are fabricated entirely by screen-printing using polymer inks from ElectroScienceLaboratory (ESL). The sensitive layer is first printed using the modified resistive RS-12113 (1k□/square) ink containing carbon black. The humidity sensitive nanoparticles $Fe[(Htrz)_2(trz)]BF_4$, are incorporated in the carbon black-epoxy matrix with the appropriate weight percentage in order to maintain correct rheological properties for screen-printing. Using this modified RS-12113 ink, layers 15 mm long and 3 mm wide are printed on an alumina substrate. After printing, the resistive ink is dried at 120°C for 20 min and then cured at 230°C for 6 min using a vapour-phase equipment [8]. The final cured sensitive layers are approximately 20 µm thick. After the sensitive layer deposition, Ag contacts are screen-printed using the 1901-S epoxy ink cured at 120°C for 20 min (see Fig.1). In parallel, reference samples of identical shape and thickness are also fabricated. These are based on the RS15113 ink and included carbon black but not the Fe(II) spin crossover compound.

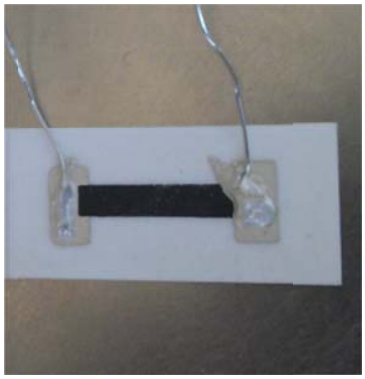

Fig. 1. Photograph of the screen-printed 15 x3x0.02mm^3 carbon-black and Fe(II) spin crossover compound hybrid films with Ag electrical contacts layers .

3. Tests under humidity

The sensors are placed in an air-tight measurement rig in which computer-controlled liquid and gas mass flow meters are used to adjust the moisture level in synthetic air. Response and recovery cycles to increasing moisture levels (from dry to 80% R.H., at 30ºC) are obtained for carbon black sensors with and without the Fe(II) spin crossover compound (see Fig. 2, 3 and 4).

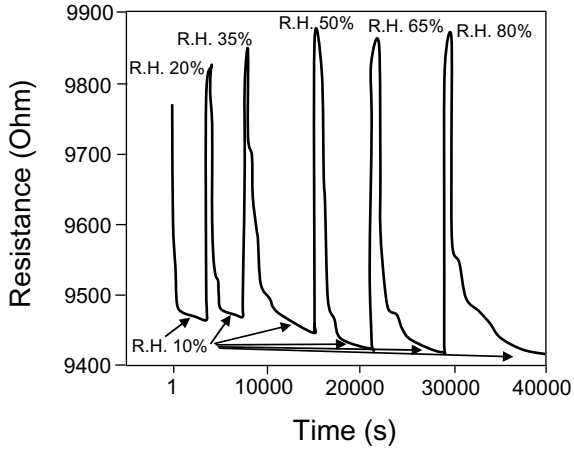

Fig. 2. Response and recovery cycles to increasing moisture levels for carbon black sensors with the Fe(II) spin crossover compound.

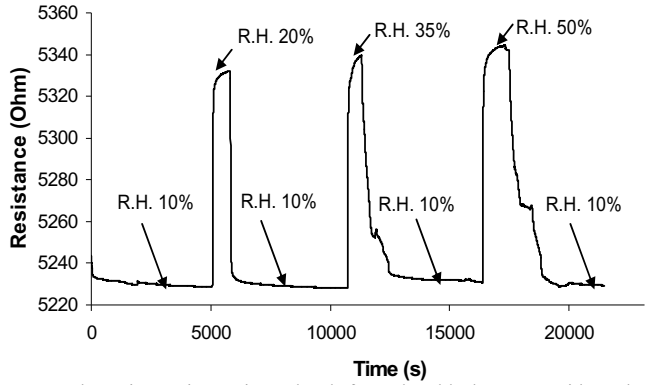

Fig. 3. Response and recovery cycles to increasing moisture levels for carbon black sensors without the Fe(II) spin crossover compound.

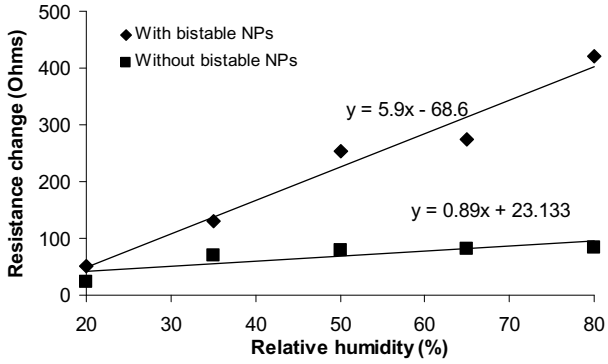

Fig. 4. Resistance change of sensors having (and lacking of) bistable nanoparticles when relative humidity is changed stepwise from the baseline value (10% @ 30ºC) to 20, 35, 50, 65 and 80%. The slope of the linear fits indicates sensitivity towards humidity.

4. Conclusion

While sensors based on carbon-black only tend to response saturation at 50% R.H. levels, this effect is not seen in sensors employing the carbon-black and Fe(II) spin crossover compound hybrids. Furthermore, the latter show a 6-fold increase in moisture sensitivity. In summary, the material shows good potential for a selective humidity detection when operated at room temperature.

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