Sensors and Actuators A 156 (2009) 164–170

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Dielectrophoretic alignment of polymer compounds for thermal sensing

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ARTICLE INFO

Article history:
Received 30 September 2008
Received in revised form 24 March 2009
Accepted 26 March 2009
Available online 17 April 2009

Keywords:
Polymer compound
Dielectrophoresis
Thermal sensor
Tellurium
Nanorod

ABSTRACT

In this work polymer compounds with an electrically conducting filler material, being aligned in an inhomogeneous electric field using dielectrophoresis, were investigated. Chemically synthesized semiconducting tellurium nanorods were used as filler material. Resulting resistances of the aligned polymer compounds can be accurately tailored between 500 kΩ and 10 TΩ. The corresponding temperature behavior of the resistance was examined and showed strong dependence on the degree of alignment and on the matrix polymer used. The adjustable temperature coefficient of resistivity (TCR) has values of (−0.7. . .−4.1)%/K. Additionally, structuring techniques based on lithography and stamping processes are exemplary described and demonstrated for resistive thermal sensor elements.

1. Introduction

Polymer compounds with electrically conducting fillers are an interesting field of research concerning sensors to measure gas [1] or pressure [2] and for actuators [3]. Those polymer-based systems benefit from advantages like (i) cost-effectiveness, (ii) simple processing, and (iii) tailoring of material properties.

Conventional homogeneous polymer compounds show statistical distribution of the filling material leading to a typical percolation behavior. Therefore, the required amount of filler to create a conducting network is comparatively high causing problems with the technological processability of the polymer compound.

This problem can be solved by using rod-like filler material and by aligning the rods in the desired direction, so that the amount of filler required establishing a conducting network can be reduced significantly.

Alignment of nanorods or nanotubes, for the latter especially carbon nanotubes, were performed with various techniques like alignment during the growth process [4], by a template method, using porous alumina structures [5], or with extreme magnetic fields [6].

In this work the alignment process in an electric field is studied. The corresponding effect called dielectrophoresis is based on the polarizability of a material in an electric field. The resulting dielectrophoretic force is described by the equation

$$F_{\mathrm{Dep}} = 2\pi V_P \varepsilon_m \,\mathrm{Re}\{K(\omega)\}\nabla|\vec{E}|^2 \quad \text{with} \quad K(\varpi) = \frac{\varepsilon_p^*(\omega) - \varepsilon_m^*(\omega)}{\varepsilon_p^*(\omega) + 2\varepsilon_m^*(\omega)}, \quad (1)$$

where V_p is the volume of the particle, ε_m the permittivity of the surrounding media, ε_p the permittivity of the particle material and E the electric field strength. The relation between ε_m and ε_p is expressed by the Clausius–Mossotti factor K. An attracting force of the particle results towards higher electrical field intensity if ε_p is larger than ε_m. This condition is essential for a successful dielectrophoretic alignment procedure.

In contrast to the alignment techniques described above, electrical alignment of elongated nanoparticles have major advantages: the electrodes used for the dielectrophoresis process can be used as well to characterize the particles during the subsequent application. An example for such an application under investigation is the so-called CNTFET [7], where carbon nanotubes were aligned between electrodes and used as field effect transistors. In addition, the dielectrophoretic alignment enables tailoring of the desired properties by adjusting parameters like the applied voltage, the filler content, or the surrounding media.

This work deals with the defined alignment of tellurium nanorods in the polymer poly(vinyl acetate) (PVAc) and in a novolak-based positive photoresist with respect to the application in resistive thermal sensors.

The influence of the thermal expansion of the polymer during the thermal characterization is investigated using different polymer matrix materials. The photoresist can be highly cross-linked by thermal treatment, resulting in a very hard and thermally stable phenolic resin with a coefficient of thermal expansion (CTE)

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doi:10.1016/j.sna.2009.03.033

of $5 \times 10^{-5}\,K^{-1}$ [8]. In contrast, PVAc has a much higher CTE of $28 \times 10^{-5}\,K^{-1}$ [9]. During thermal treatment we assume that neighboring inorganic filler particles are separated due to the expansion of the polymer. This lowers the resistance of the aligned compound at higher temperatures leading to a reduced absolute value of the negative temperature coefficient of resistivity (TCR). The effect should be stronger for PVAc compared to the highly cross-linked photoresist.

The filler material of choice has to fulfill the demands of the application in a resistive thermal detector. Therefore, great TCR values are of major importance. Conventional compounds with carbon nanotubes, carbon fibres, or carbon black exhibit very low absolute TCR values below −0.5%/K [10–12]. Furthermore, compounds with carbon black [13] or carbon nanotubes [14] and special semi-crystalline polymers show high positive TCR values above 10%/K. This effect is caused by the melting of the crystalline parts of the polymer accompanied by an expansion of the conducting network. Resulting electrical properties show problematic long term stability and typically a distinctive hysteresis behavior [13]. Therefore, these filler materials are not well suited for the application in a resistive thermal detector.

The chosen filler material in this work is tellurium because (i) it is a low band-gap semi-conductor with a high intrinsic negative TCR (−2.3%/K) [15] and (ii) it can be easily synthesized in nanorod form (Fig. 1), leading to higher dielectrophoretic forces compared to spherical particles.

2. Experimental

2.1. Dielectrophoresis

Tellurium nanorods were synthesized using the chemical reduction of telluric acid (H_6TeO_6) with hydrazine (N_2H_4) [16,17]:

$$2H_6TeO_6 + 3N_2H_4 \rightarrow 2Te + 3N_2 + 12H_2O.$$

Resulting nanorods are presented in Fig. 1. The SEM images show a narrow statistical distribution of the nanorods with an average diameter of 250 nm, an average length of 5 μm, and a subsequent aspect ratio of 20. The chosen synthesis procedure leads to clean surfaces of the particles that is desired for a good electrical contact.

PVAc with a molar chain length of 60,000 was supplied by Carl Roth (Germany). The used photoresist AZ 1514 was delivered by Allresist (Germany). The main solid component in this photoresist is a novolak that can be cross-linked by heating above 150 °C to a phenolic resin.

The polymer compounds were prepared by adding the desired amount of tellurium to the polymer solution. Polymer solvents used were acetone for PVAc and propylene glycol monomethyl ether acetate (PGMEA) for the photoresist AZ 1514. The suspensions were treated with ultrasonic power to yield the required homogeneous distribution of the tellurium nanorods.

Dielectrophoresis was performed as presented schematically in Fig. 2. For monitoring the alignment process by measuring the current flow a standard oscilloscope with a low ohmic resistance or a multimeter were used.

Samples for the basic electrical characterization were prepared by coating the homogeneous suspension onto a glass substrate with gold electrodes being separated by a distance of 25 μm. The use of gold or an adequate noble material as electrode material is necessary to prevent decomposition of the electrodes by electrolysis. For the dielectrophoretic alignment procedure, a sufficient mobility of the polymer matrix is important. Dielectrophoresis with the PVAc compounds were performed solvent-free by heating the sample closely beyond the melting temperature of PVAc (above 100 °C).

It is not possible to achieve the melting state of most photoresists like the used AZ 1514, because they cross-link at elevated temperatures. Cross-linking occurs either by temperature activation of the photo initiator or by a condensation reaction of the polymer backbone [18]. Consequently, the dielectrophoretic alignment procedure has to be performed in the dissolved polymer compound. Finally, these samples were annealed (180 °C) for 1 h to remove the solvent PGMEA and to execute a significant cross-linking process.

Additionally, for comparison purpose, an aligned sample of pure tellurium without a polymer matrix was investigated. For this purpose, a homogeneous suspension of 0.1 wt.% tellurium in ethanol was used. The solvent ethanol was evaporated after the alignment process at room temperature.

2.2. Structuring of sensor elements

The patterning of individual pixels for conventional resistive thermal sensors, especially for sensor arrays like microbolometers, is typically a complex technology procedure. By using the technique described in this paper it is possible to realize separate sensor elements within one homogeneous layer, just be aligning the nanorods at the desired spots. However, the quality of thermal sensors correlates with both its low thermal capacitance and low thermal conductance. Therefore, it is desirable to reduce the total mass of the thermal sensor elements by using well suited patterning techniques for the presented polymer compounds.

Patterning of the polymer compound with PVAc can be achieved by a stamping technique using an elastic silicone mold of poly(dimethylsiloxane) (PDMS). This technique is similar to the nanoimprint lithography (NIL) technology being investigated intensively at present to cross the current resolution limits in lithography. With the NIL technique structures down to 10 nm can be defined [19].

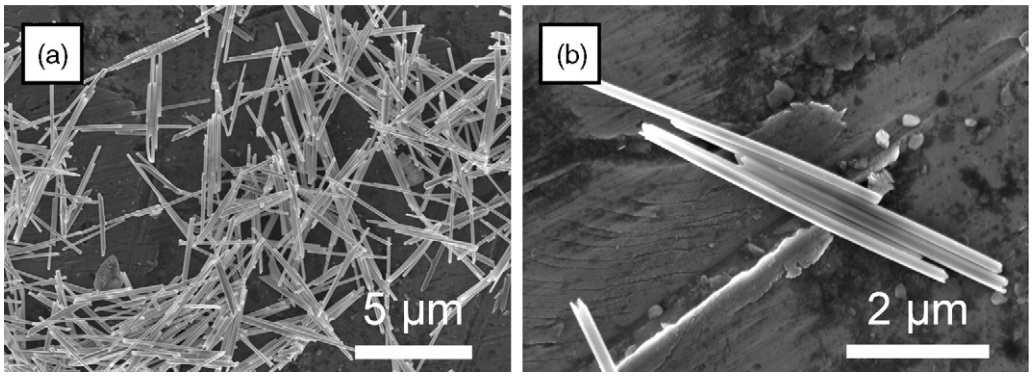

Fig. 1. SEM images of synthesized tellurium nanorods.