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Evolution of nano-junctions in piezoresistive nanostrand composites

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ABSTRACT

When nickel nanostrands (NiNs) are embedded inside of highly flexible silicone, the silicone becomes an extremely piezoresistive sensor capable of measuring a large dynamic range of strains. These sensors experience an increase in conductance of several orders of magnitude when strained to 40% elongation. It has been hypothesized that this effect stems from a net change in average junction distance between the conductive particles when the overall material is strained. The quantum tunneling resistance across these gaps is highly sensitive to junction distance, resulting in the immense piezoresistive effect. In this paper, the average junction distance is monitored using dielectric spectroscopy while the material is strained. By incorporating new barrier height measurements of the base silicone material from a nano-indentation experiment, this experiment validates previous assumptions that, on average, the junctions between NiNs decrease while the sample is strained, instigating the large piezoresistive effect. The nature of the material's response to strain is explored and discussed.

1. Introduction

In recent years there has been a push for the development of multifunctional composite materials that integrate physical properties such as flexibility and durability with other desirable properties in order to provide new alternatives to traditional materials. Such composites can benefit greatly from what may be generically termed the "nano-effect"; for example, the unexpected properties of nano-scaled fillers that exhibit unusual, and often extreme, properties [1,2]. Nano-fillers are being used in many cases to improve mechanical properties such as toughness, modulus and strength with unexpected improvements in many cases [3–5]. One particular area of active research relates to the development of conductive composites made with nano-fillers [6–10].

Conductive composites have shown particularly interesting multifunctional properties that often enable them to be used in sensing situations [11–17]. One extreme example involves a silicone/nickel nanostrand nanocomposite material that exhibits a very large piezoresistive response to applied strain, arising from nano-effects between the conductive fillers. Related materials shows promise as large strain sensors, undergoing an unusual increase in conductivity as tensile strain is applied [18–22].

Attempts have been made by Johnson et al. to develop a numerical model that can both explain and predict the behavior of this material under strain [23,24]. Johnson's model predicts that quantum mechanical effects play a principal part in the change of resistivity in the composite material, as opposed to other proposed theories such as density or alignment changes of conductive filler [25]. It is proposed that the ultra-low density clusters of nickel nano-particles are pushed together as they are embedded into the polymer matrix. A nano-layer of adsorbed polymer produces a tiny gap, or junction, between the clusters, across which electrons can potentially pass via a quantum tunneling mechanism [26]. As the macro-scale material is deformed, small changes in these nano-junctions produce exponential changes in the tunneling resistance across them, leading to paths of low resistance across the sample and the related extreme piezoresistivity.

The Johnson implementation of the quantum tunneling/percolation model uses a simple Monte-Carlo simulation of the evolving nano-junctions between conductive filler particles in the material. This stochastic representation of the nanojunctions is combined with a standard percolation model for resistance in conductive

Abbreviation: NiN, nickel nanostrand.
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networks [24,27]. While the resultant approach shows promising agreement with general resistance trends, many parameters in the simulation were approximated using incomplete assumptions, and current models of gap evolution are extremely simplistic [28,29]. Perhaps the most critical information missing from all such models is measured data for the junction gap (or junction distance) in the composite. In an effort to fill in this missing information, this paper directly measures the average junction distance between the nickel nanostrands (NiNs) in composite gauges undergoing various degrees of strain.

A previously developed method to measure average nano-junction distances was adapted to provide the data required to improve the existing model [30]. The composite material was strained inside an impedance analyzer, facilitating measurement of the changing dielectric constant of the material. The dielectric constant was used to calculate the average junction distance. The results of this experiment will be used to continue to develop the multiscale model, and this novel experimental method could be applied by other research teams trying to understand the conductive nature of other nanocomposite materials. This method has limitations as it only provides a single number average junction distance, but the trends observed provide strong evidence for both the simple quantum tunneling effect predictions and the more advanced percolation model.

Most of the work in the aforementioned theories is based on quantum tunneling equations. The quantum tunneling barrier height of a material (the resistance that a material naturally has to certain quantum effects) is critical for the accuracy of these calculations. Previous work pioneered a new method to properly measure this barrier height involving precision nanoindentation with a conductive probe [24,27]. This paper utilizes recent refinements of the technique as outlined by Koecher et al. [30] to provide improved and robust barrier height results on the material.

2. Experiment

2.1. Materials

A single sample of catalyzed Sylgard 184, a common commercial silicone produced by Dow Corning®, was used for the barrier height measurement tests (see Section 2.2). Sylgard 184 is a nonconductive, flexible silicone base useful for making highly deformable sensors. Nickel substrates for this test were purchased from National Electronic Alloys®, flattened, sanded and polished with a series of increasingly fine slurries (including colloidal silica). After a final electropolishing step, the substrates were cleaned with acetone and ethanol. Immediately prior to film deposition, atmospheric plasma etching was used as a final cleaning step. The silicone was deposited onto the substrates and cured by baking at 110 °C for 18 h. Because the area used in nanoindentation is extremely small, it was possible to reuse the same sample for many tests.

Samples of the nanocomposite conductive material used in the junction distance tests (see Section 2.3) were prepared by mixing conductive particles with Sylgard 184. The conductive fillers were nickel nanostrands—high aspect ratio nanoparticles with a unique bifurcated structure. They are made by Conductive Composites, LLC through a proprietary chemical vapor deposition (CVD) process. This process creates a highly porous mass with a volume fraction in air of less than 1%. The porous nanostrand mass is broken apart and mixed into the samples. This experiment used volume fractions in polymer ranging from 7% Ni to 13% Ni. The composite was then cast into a long, wide, thin aluminum mold and, after being warmed to 75 °C to encourage polymerization, was allowed to cure at room temperature for several days. Fig. 1 shows a cluster of NiNs inside of a cured silicone matrix as photographed in a SEM.

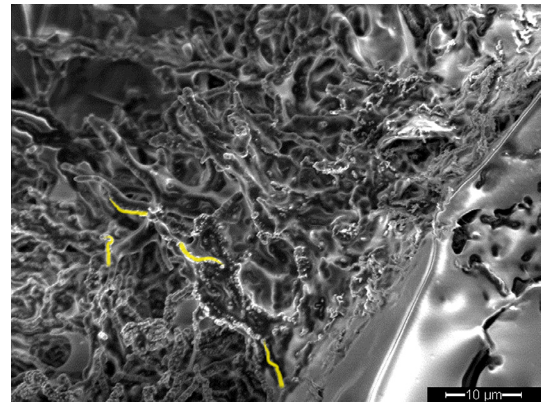

Fig. 1. A high density cluster of NiNs inside the silicone matrix. Several nanostrands have been highlighted in yellow. The smooth, reflective material on the right side of the picture is matrix material with few or no NiNs embedded along the border of the material. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Barrier height measurements

A series of nine tests were performed in order to determine the quantum tunneling barrier height of the Sylgard 184. Measurement of the barrier height was performed following the method of Koecher et al. [30]. Briefly, a Hysitron nanoindenter was operated in the nanoscale electrical contact resistance (nanoECR®) mode, which provides continuous measurement of electrical current during indentation by using a conductive stage and boron-doped conductive diamond tip with a 5 V bias voltage. As the tip moves downwards through the silicone towards the Ni substrate, the current suddenly increases from zero when electrons are able to tunnel through some minimal thickness of the polymer. This jump in current is approximately linear with probe position and a linear regression can be used to calculate impedance as a function of distance between the tip and the substrate [30]. The barrier height (λ) is then calculated from the slope (m) of that function as shown in Eq. (1). For more details, the reader is referred to the already published work.

$$\lambda\ (\text{eV}) = \left(\frac{m}{1.025}\right)^2 \tag{1}$$

Note that only the initial linear increase in current is used, because after several nm the indenter has pushed through the polymer and into the conductive substrate. After this point, variations in the current are a function of indenter geometry and substrate deformation. The barrier height calculations are calibrated by a standard indent into gold, wherein the barrier height of air is measured and verified against literature reports.

2.3. Junction distance

The nanocomposite material consists of a network of conductive strands separated by junctions that possess both a characteristic resistance and capacitance. Previous studies in nanocomposite materials have modeled the nano-junctions between particles of the filler material as a parallel resister and capacitor circuit [29,31,32]. The relaxation frequency of this network relates to both the size and dielectric properties of the junctions. Previous analysis has produced the following equation that correlates the relaxation