Cellulose Nanofiber Composite Substrates for Flexible Electronics

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Flexible electronics have a large number of potential applications including malleable displays and wearable computers. The current research into high-speed, flexible electronic substrates employs the use of plastics for the flexible substrate, but these plastics typically have drawbacks, such as high thermal expansion coefficients. Transparent films made from cellulose nanofibers have low thermal expansion and thus the potential to serve as substrates for flexible electronics. Here we present the results of using a cellulose nanofiber composite substrate for flexible electronics. While the initial processing procedures need improvement to reduce the film surface roughness and composite thermal expansion coefficient, a working prototype was built and is reported here.

Introduction

The demand for mobile computing continues to rise, and more than 1.5 billion mobile devices were shipped in 2011 [1]. As mobile computing becomes more powerful and pervasive, the roles that electronic play in daily life also changes. Mobile computing devices have already made significant impact on the print media market, and displacement of printed media by electronic devices is expected to increase. Flexible electronics especially have potential applications as displays, solar cells, smart cards, radio frequency (RF) tags, and medical implants [2].

Recent advances have demonstrated enormous potential for high-speed flexible electronics [2,3]. Researchers recently demonstrated the ability to transfer silicon nanomembranes onto flexible plastic substrates to create thin-film transistors having a 12 GHz maximum oscillation frequency [3]. Such speeds suggest a wide range of potential applications, including RF identification devices and wearable radios.

While enhanced transfer and lithography techniques are able to result in reduced feature sizes, the large thermal expansion of plastic substrates presents a challenge in terms of dimensional stability and thus long-term, practical performance of high-speed flexible electronics. Cellulose nanofiber composites have good mechanical properties and low thermal expansion [4-6] and have the potential to serve as substrates for flexible electronics. Researchers have previously demonstrated the use of cellulose nanofiber composites as substrates for low speed flexible

displays [6]. However, these devices rely on the deposition of organic light-emitting diodes deposited onto flexible substrates, resulting in devices that have severe performance limitations. The first demonstration of cellulose nanofiber composites as a substrate for flexible electronics with the potential for high-speed applications is presented here.

Furthermore, as electronics become more ubiquitous, the need for incorporating environmentally benign materials increases. In the United States alone, 129 million mobile devices were disposed in 2009, and less than 12 million of those were recycled [7]. The amount of electronic waste continues to increase and is a serious environmental problem in many countries. Therefore use of bio-derived and biodegradable materials, such as cellulose nanofibers, in electronics is becoming increasingly important and has the potential to reduce the environmental impact of electronic devices.

Experimental

Cellulose Nanofiber Composite

Cellulose nanofibers (CNF) were prepared by the enzymatic and mechanical fibrillation of bleached Kraft eucalyptus pulp as previously described in detail [8]. The coarse fibers were first treated with multiple enzymes, then they were refined in a Microfluidizer processor from Microfluidics (Newton, MA). The nanofiber suspension was then filtered in an ultrafiltration apparatus with polytetrafluoroethylene (PTFE) membranes with 0.1 micrometer pore sizes. The filter cake was then sandwiched and dried between layers of release paper, filter paper, and caul plates at room temperature under a pressure of approximately 2-3 psi for three days. The films were then dried for several hours at 130 °C prior to forming into composites.

Cellulose nanofiber-epoxy composite were created by laminating CNF films with a bisphenol A-based epoxy resin system from The Dow Chemical Company. A low viscosity epoxy resin (D.E.R. 324) was mixed with a flexible epoxy resin (D.E.R. 732) at a 70/30 ratio and mixed with stochiometric amounts of amine-based curing agent (D.E.H. 26). The epoxy was brushed onto one side of the cellulose nanofiber film, and the coated film was pressed at 130 °C for ten minutes at a set point of 100 psi. The coating and pressing was repeated for the second side.

Transistor Fabrication and Testing

The fabrication of thin-film transistors using silicon nanomembranes (SiNM) on flexible substrates has been previously described [9], and the process employed for this study is summarized here. Nanomembrane strips were first prepared from commercially available silicon-on-insulator wafer substrates. The source and drain contacts were then made on the nanomembranes prior to deposition to the CNF composite substrate. The CNF substrate was cleaned in acetone for five minutes, then a layer of epoxy (Microchem SU-8-2) was spun coated

onto the CNF composite. The SiNM was then transferred onto the uncured epoxy layer, which was subsequently cured by a combination of UV light and heating at 115 °C. The device was isolated by dry plasma etching with SF_6. The gate stack was formed by e-beam evaporation followed by an acetone washing lift-off process and consisted of 130 nm of amorphous silicon monoxide (SiO), 5 nm of Ti and 170 nm of Au. Finally, the source and drain metal contacts were created.

The transfer and movement of the nanomembrane strips were evaluated by optical microscopy. To estimate the thermal expansion of the substrate, the variation in gaps between the strips was measured and compared before and after heating at 95 °C for 6 min and 115°C for 3 min, which represent heating duration and limits during fabrication. The DC characteristics of the fabricated transistor were also tested.

Results and Discussion

The fabrication of a working thin-film transistor (TFT) on CNF substrate presents a number of challenges compared to polymer substrates. First, a well-defined automated process for creating CNF films does not exist, so the films often have numerous imperfections and large surface roughness. In some cases, this roughness was measured to be as high as ten micrometers, which is unsuitable for fabricating nanometer scale devices. Prior to successful fabrication of the device, numerous attempts and optimization efforts were made. Initially, neat CNF films were used. However, this resulted in difficulty in transferring the SiNMs. Transfers were attempted using a variety of SU-8-2 thicknesses and spin coating conditions, but even the most successful of these attempts on neat CNF films produced less than desirable transfer rates, as shown in Figure 1. Another challenge is that without treatment, the CNF films are subject to swelling during

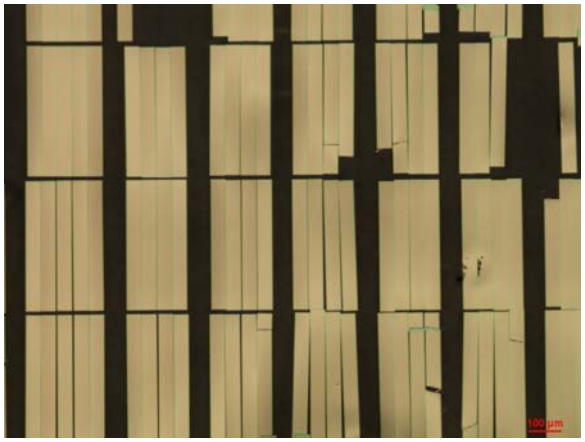

Figure 1: SiNM transferred to neat CNF films

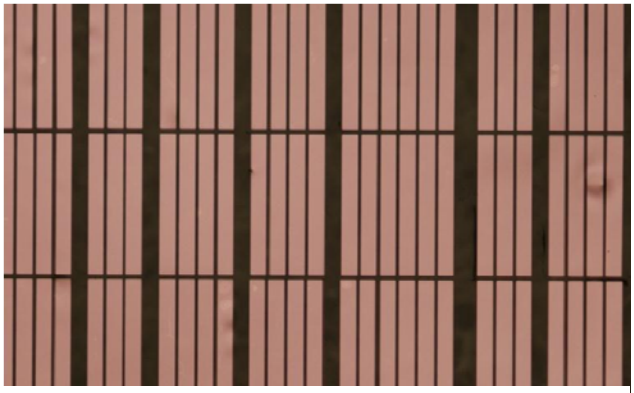

Figure 2: SiNMs transferred to CNF-epoxy films

cleaning and other fabrication stages in which liquid chemicals are used. Furthermore, neat CNF films appeared to have a tendency to absorb the low viscosity epoxy used to attach the SiNM to the films.

To eliminate some of these problems, the CNF films were formed into laminate composites with epoxy prior to transfer. The surface roughness of these composite films was considerably less than the original neat films. The neat films measured approximately 100 µm in thickness, and the laminate thickness was approximately 200 µm. This facilitated transfer of SiNMs, as shown in Figure 2. In this case, the transfer yield was 100%. The composite film was also soaked in acetone for at least five minutes, after which no noticeable deterioration of the composite was noticed, further indicating that a CNF-epoxy composite is suitable for use as a flexible electronic substrate.

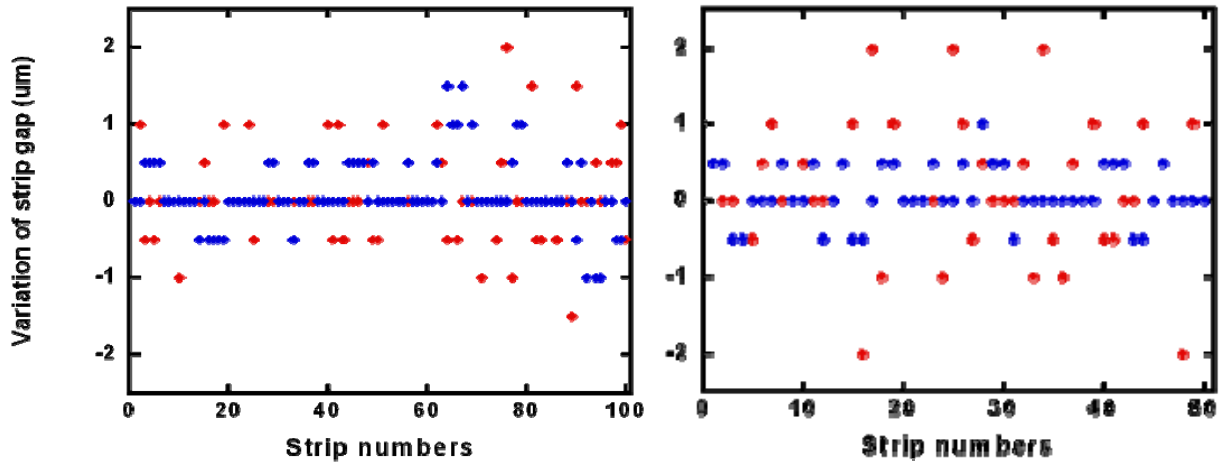

Figure 3: Thermal expansion measured by variation of SiNM strip gaps before (left) and after (right) heating; the red markers represent vertical alignment and the blue represent horizontal

The thermal stability of the composite is crucial since movement of the silicon nanomembranes, and thus transistors, could easily result in device failures. The movement of the nanomembranes was examined by measuring the variation of strip gaps before and after heating. The plots are shown in Figure 3. For every 500 µm, about 0.5-0.7 µm of strip movement was measured. This is higher than preferred and is due to the large amount of epoxy in the composite and adhesive layer, but the movement was sufficiently low that the strips did not overlap. Therefore, transistor could be fabricated on the nanomembranes transferred to the flexible CNF composite film.

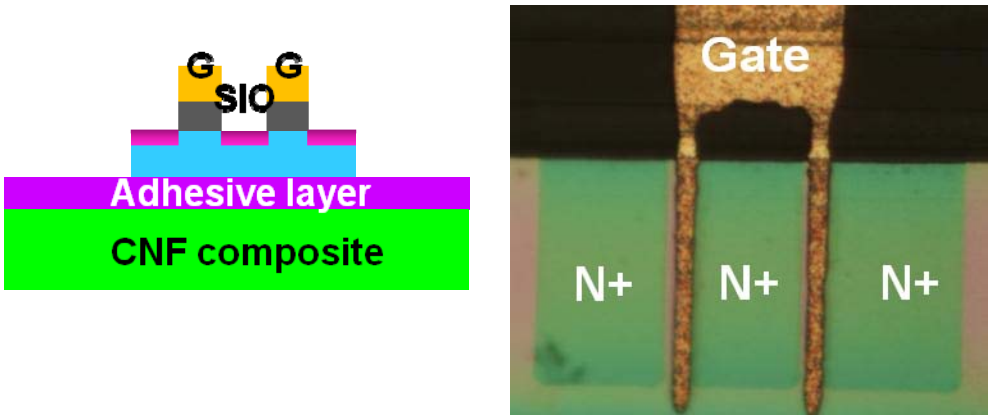

Figure 4: Schematic and micrograph of the gate stack. N+: doped area; G: gate.

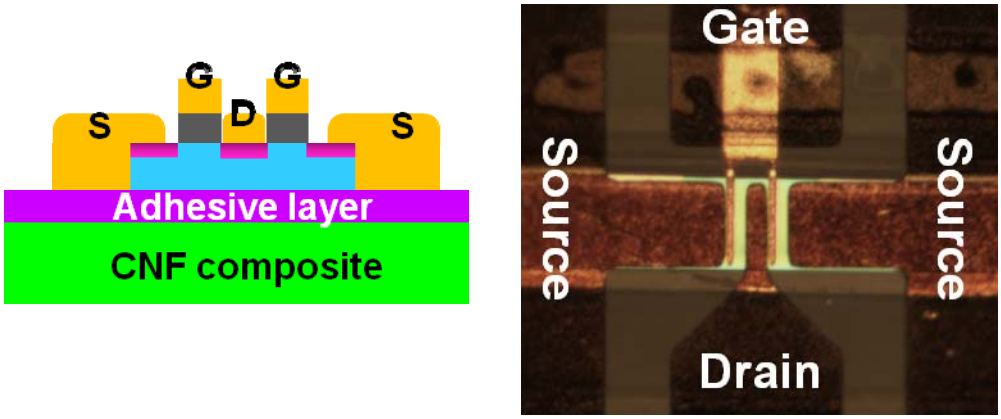

Figure 5: Schematic and micrograph of the final TFT device. S: source; G: gate; D: drain.

Schematics and micrographs of the final stages of the device are shown in Figures 4 and 5. Figure 4 shows the gate stack, and Figure 5 shows the device after the source and drain are deposited. The electrical characteristics of the device are shown in Figure 6. The drain current measured here was considerably lower than typical values, which range from 5 – 20 µA under similar bias conditions. This low current is possibly due to ion diffusion away from the surface in the doped n+ layer, although further investigation is needed to verify this.

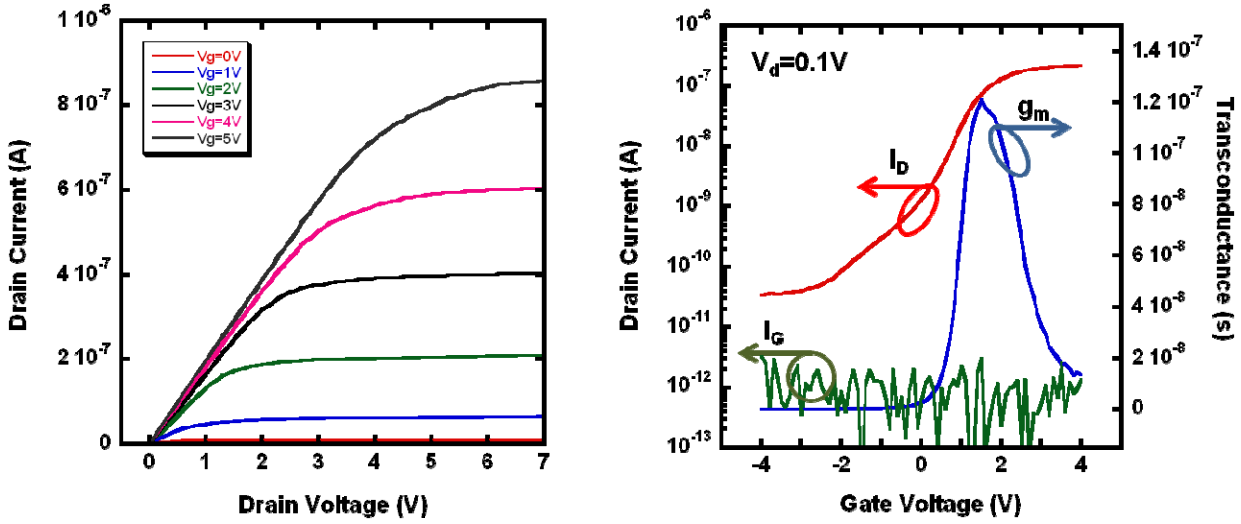

Figure 6: Electrical characteristics of the device. V_g: Gate voltage; I_d: drain current; g_m: transconductance; V_d: drain voltage.

Conclusions

The first example of using cellulose nanofiber composite substrates for flexible electronics made by transferring silicon nanomembranes was demonstrated by fabricating and testing a working thin-film transistor. The cellulose nanofiber composite showed good chemical and thermal resistance necessary for electronic fabrication. Some challenges remain as the use of resin in this initial device resulted in larger than expected thermal expansion of the composite substrate. However, the use of cellulose nanofibers as a sustainable component for high-speed flexible electronics is extremely promising.

Acknowledgments

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