A novel transparent air-stable printable n-type semiconductor technology using ZnO nanoparticles

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Abstract

We report on a novel, air-stable, printable, transparent, NMOS semiconductor technology using soluble ZnO nanoparticles. We demonstrate solution-processed transistors with mobility > 0.1cm^2/V·s, which is the highest solution-processed NMOS mobility reported to date. The air-stability and transparency make this device an ideal candidate for low-cost printed displays and CMOS circuitry.

Introduction

There is great interest in printing for realizing low-cost electronics. Based on various reported cost models, printed electronics is expected to be two to three orders of magnitude cheaper per unit area than conventional semiconductor manufacturing flows, albeit at a higher cost per transistor (1). Therefore, for area-constrained applications such as displays and low-frequency RFID tags, printed electronics has garnered substantial interest. Most printed transistors to date make use of organic semiconductors with mobilities between 0.01 and 1 cm^2/V·s, which is adequate for some displays, and approaching the realm of performance required for RFID tags (2). Several deficiencies remain, however. Most printable semiconductors today are p-type; available n-type semiconductors have mobilities <10^{-2} cm^2/V·s, which is generally considered to be too low for most printed electronics applications. This prevents the use of low-power CMOS circuits and also increases transistor count and circuit complexity. Most printable semiconductors also have poor air-stability, complicating packaging and degraded device lifetime. Additionally, many printable semiconductors, including organics and chalcogenides are toxic, and their integration into disposable circuits is problematic. Finally, for display applications, none of these materials is transparent. This is problematic, since, due to the low mobility of printed devices, it is generally desirable to use multi-transistor pixels or wide pixel transistors to maximize display brightness and contrast. Since all printed devices to date are opaque or semi-transparent at best, pixel aperture ratio is sacrificed when using any of these techniques. This in turn degrades display brightness and energy efficiency.

The need therefore exists for a printable NMOS material offering improved mobility, air-stability, low toxicity, and optical transparency. For the first time, we report on such a material. We have developed a novel printable semiconductor using 3nm zinc oxide nanoparticles. We take advantage of the reduction in sintering temperature observed for nanoparticles in order to produce thin films at reduced temperatures (3). These particles have a 105ºC melting point and are soluble and printable. By annealing solution-processed films at plastic-compatible temperatures, semiconducting ZnO (a comparatively benign material routinely used in antifungal ointments) films are formed. NMOS TFTs fabricated using these films, which are optically transparent, have mobilities > 0.1cm^2/V·s. Due to their transparency, they may be sized without brightness tradeoffs in flexible display applications. Because the material is an oxide and is therefore unreactive in air, ambient exposure over long periods of time has no effect on performance; this is in great contrast to most other printable semiconductors. This therefore represents a major step towards the realization of printed CMOS integrated circuits for low-cost electronics.

Experimental Details

ZnO nanoparticles were synthesized by reacting zinc acetate with NaOH in 2-propanol. After 15 minutes, dodecanethiol encapsulant is added. After 2 hours, the resulting alkanethiol-encapsulated ZnO nanoparticles are collected and purified. The resulting particles consist of ~3nm ZnO crystals surrounded by a monolayer of dodecanethiol encapsulant. The size of the particle is determined by the time of addition of the encapsulant and the relative concentrations of the encapsulant and metallic precursor. The encapsulant serves to ensure the particle growth is self-limited to 3nm, prevents subsequent particle agglomeration, and allows the solubilization of the particles in numerous common organic solvents. The process for particle synthesis is shown schematically below (Fig. 1)

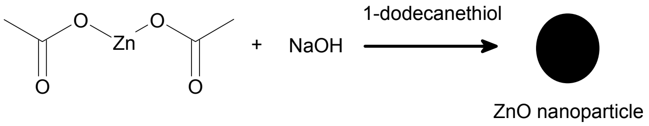

Fig. 1: Scheme used for synthesis of ZnO nanoparticles.

The diameter of the resulting particle is verified to be approximately 3nm by transmission electron micrograph (Fig. 2).

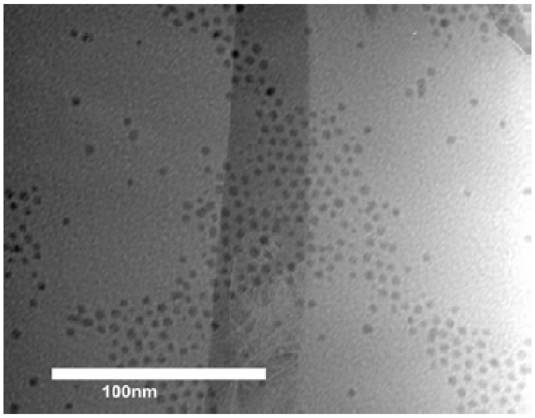

Fig. 2: TEM of zinc-oxide nanoparticles, showing tight size distribution. The particles have an average diameter of 3nm, and are encapsulated with 1-dodecanethiol.

Heating experiments were performed to verify that the encapsulant evaporates and the particles sinter at ~105ºC in air; this material is therefore potentially plastic-compatible, assuming the remainder of the process is also optimized for use on plastic. Electrical performance was evaluated by fabricated bottom-gated transistors with N+ silicon gates, 100nm thermal SiO_2 gate dielectrics, and evaporated gold S/D pads. The ZnO particles were spun-cast in chloroform and annealed at 150ºC. A conventional 400ºC forming-gas anneal was performed to passivate dangling bonds; this step may be replaced with plasma hydrogenation in a plastic compatible process. The final thickness of the zinc oxide is 40nm, while the initial thickness was 80nm (Fig. 3), as measured by profilometry. This thickness reduction is evidence of the sublimation of the encapsulant and the sintering of the particles to form a film. Physically, the film also undergoes substantial changes during this sintering process, going from a powdery film that is easily washed off in solvents to a brittle, glassy-film that is impervious to solvent treatments.

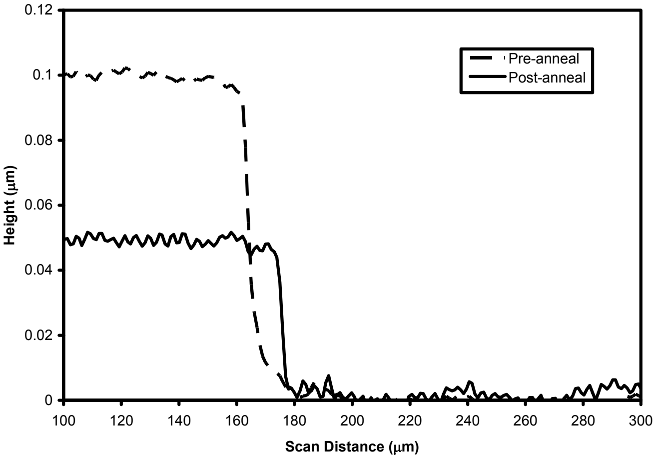

Fig. 3: Profilometry scans showing thickness reduction after annealing; this thickness reduction is caused by the encapsulant removal and particle sintering processes.

Results

Zinc oxide is an n-type semiconductor with poor inversion behavior. Therefore, the transistors are operated as accumulation-mode NMOS devices, and show excellent electrical characteristics (Figs 4, 5).

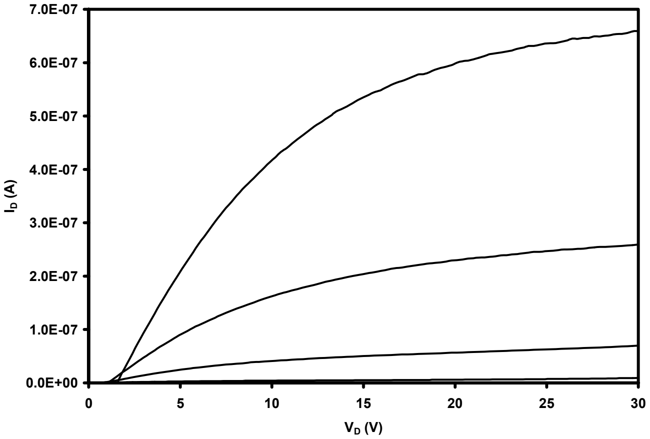

Fig. 4: Output characteristics of a typical device (W/L=20/10 µm), showing excellent characteristics. The offset in the zero-intercept is due to gate leakage and S/D barriers.

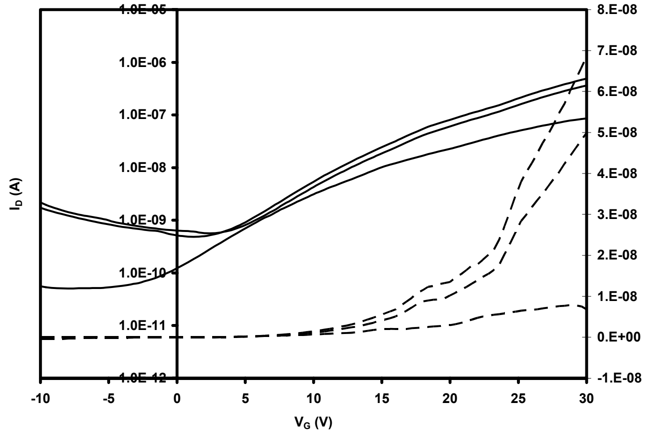

Fig. 5: Transfer Characteristics of a typical device (W/L=20/10 µm). The lack of saturation in the mobility is due to the large contact resistances in the device.

The on-off ratio is $>10^3$ and the field-effect mobility is typically in the range of 0.1- 0.2 cm^2/V-s. These are the highest mobilities ever reported from a solution-processed NMOSFET. This high performance is achieved despite the large-barrier expected to exist (and apparent from the electrical characteristics) between gold and ZnO. The large bandgap of ZnO vs. the large workfunction of Au indicates that a large barrier should exist at the S/D electrodes due to the formation of ZnO/Au schottky junctions. Evidence for this is seen in the convex turn-on characteristics in the low-V_{DS} portion of the I_D-V_D curves. This in turn dramatically degrades performance. Use of appropriate contacting materials should enhance performance even further.

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The viability of accumulation-mode devices may be analyzed using scaling. Since accumulation mode devices do not provide a large barrier to current flow in the bulk of the semiconducting film, they are prone to short channel effects. The devices herein show some V_T roll-off (Fig 6), but generally show good characteristics down to 5μm (Fig 7, 8).

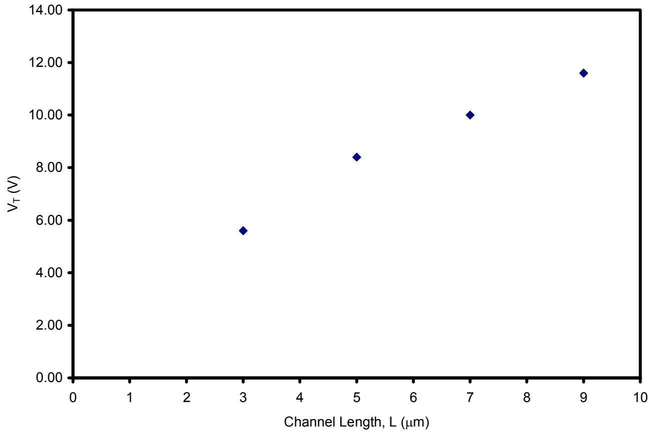

Fig. 6: V_T Roll-off characteristics. The long-channel V_T is ~12V.

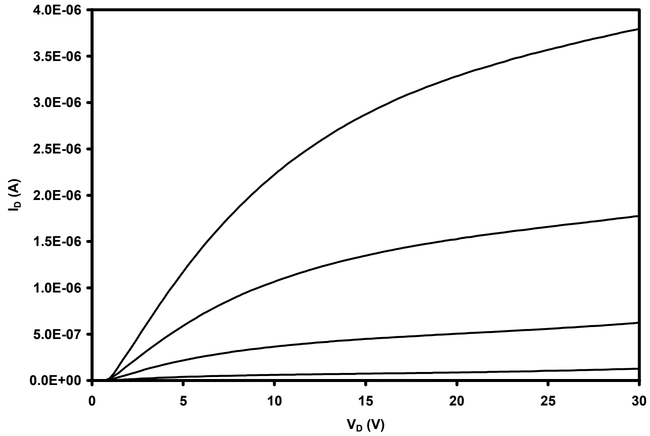

Fig. 7: Output characteristics for a 100μm/5μm device

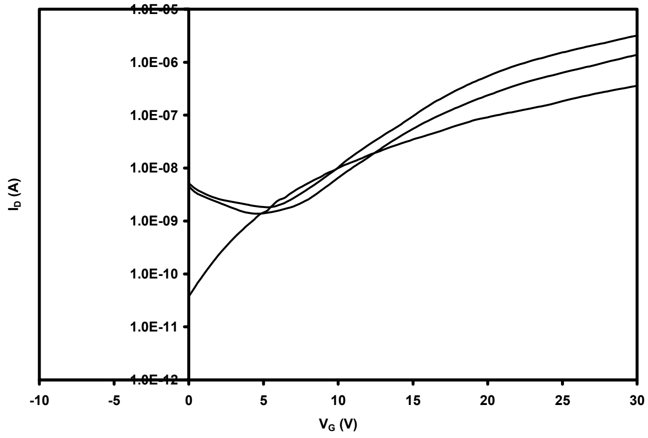

Fig. 8: Transfer characteristics for a 100μm/5μm device

Only when the channel length was reduced to 3μm did we see significant scaling related degradation (Figs 9, 10). These reasonably good scaling characteristics of these devices are likely due to two reasons. First, the use of a relatively thin channel films (~50nm) generally suppresses sub-surface leakage. Second, the relatively large source-side barrier likely suppresses DIBL, albeit at the expense of drive current and transconductance.

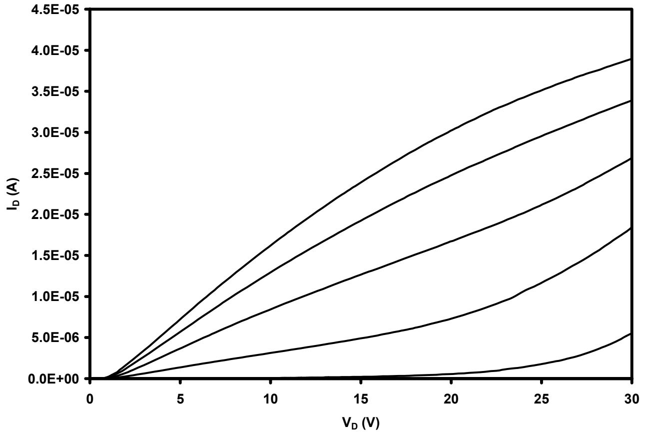

Fig. 9: Transfer characteristics for a 100μm/3μm device

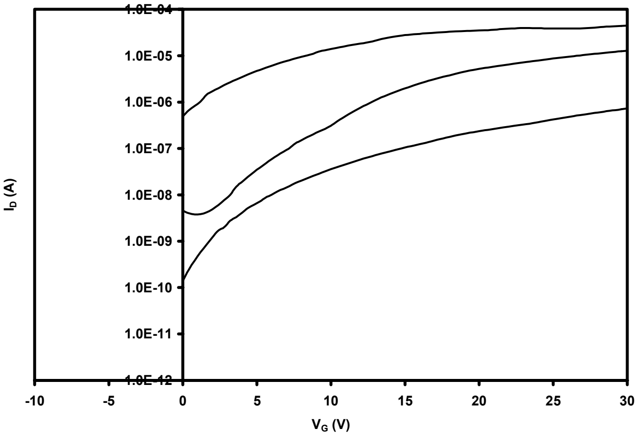

Fig. 10: Transfer characteristics for a 100μm/3μm device

Optical transparency of the zinc-oxide films was measured and found to be >93% in all samples. No degradation in performance was seen over a three month period of the devices being exposed to air. It should also be noted that all relevant device processing was performed in air, unlike most other printed electronics technologies, which require the use of inert ambients.

Discussion

The availability of a viable NMOS printable semiconductor is very importance for printed electronics. Currently, virtually all circuit implementations make use of PMOS only, complicating design and increasing power consumption. The few demonstrated CMOS implementations typically suffer from substantial performance degradation due to the typically weak NMOS transistor This is problematic, since most low-cost electronics applications will be portable (such as low-cost displays) or power starved (such as RFID tags). The availability of a suitable NMOS material will allow the realization of printed CMOS circuits, offering design simplicity and reduced power consumption. The transparency of zinc oxide also has an important benefit for displays. Given the low mobility of printed semiconductors, printed displays typically make use of pixel architectures involving wide transistors and/or multiple transistor pixel schemes. Such designs reduce the pixel emissive area, since the transistors themselves block a portion of the light. By using a transparent device, it is possible to achieve high currents without sacrificing brightness. To date only printed transparent conductors and dielectrics have been demonstrated; semiconductors have been a missing element. The technology demonstrated here fills this gap. Since the conduction band edge of ZnO is reasonably well-aligned with ITO, it is expected that high performance transparent devices should be realizable using this technology. This will enable the demonstration of active matrix displays offering high-brightness at low power while still maintaining low-fabrication cost through printing. Furthermore the stability of the compound in air when compared to many other printable semiconductor materials makes it attractive for even general applications. Unlike organic-based printed electronics and also unlike previously reported nanoparticles-based printed electronics systems (such as CdSe, etc.), the ZnO system is inherently oxygen-compatible and air-stable. Therefore, all processing may be performed in air and the need for highly oxygen exclusive barrier and encapsulation layers is also reduced. This should substantially simplify the overall process while increasing device stability. Given that poor device stability has historically been one of the major concerns hindering the deployment of printed electronics, the ZnO system is a particularly attractive candidate for printed electronics in this regard. Further optimization of the process, in particular the contacts and the annealing methodology should enable the achievement of substantially improved performance and the realization of a plastic-compatible process flow.

Conclusion

We have demonstrated the highest mobility solution-processed NMOS devices to date using soluble ZnO nanoparticles. Mobilities as high as $0.2\mathrm{cm^2/V\cdot s}$ have been realized using this air-stable, non-toxic and transparent material. This should enable the realization of all-printed CMOS low-cost electronics and low-cost flexible displays.

References

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