Developing Functional Inks for Direct-Write Systems

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Abstract

The field of Flexible Printed Electronics (FPE) carries great potential in reducing manufacturing costs and increasing versatility. The purpose of this research is to explore various ink chemistries and their suitability for deposition with regards to FPE. Titanium ceramics and silver-titanium-iron nanoparticles were utilized for their potential photocatalytic properties. The resulting inks experienced phase separation or hydrolyzed upon exposure to moisture, suggesting that a surfactant-based synthesis would better improve the inks' durability.

Keywords: Thin Film, Titanium Dioxide, Nanotube, Photocatalysis

1. Introduction

Researchers in various fields are actively pursuing direct-write deposition technologies as critical components in various applications, ranging from consumer electronics to medical implants. Direct-write deposition is a form of physical deposition that includes inkjet and aerosol spray methods, in which functionalized "inks" are deposited on a substrate. This procedure can be accomplished in ambient conditions, allowing for the use of flexible substrates as the basis for FPE. Among the various advantages of direct-write technologies, the reduced cost and potential for FPE are among the most significant. However, the lack of a variety of well-established ink formulations has led to an effort by academia and industry alike to develop the necessary functional inks.

Organometallic Ti-based inks were pursued for a number of reasons. First, the ability to decompose the metal oxide via certain conditions (in this case, exposure to moisture) gave the user additional control over the properties of the material; it allowed the user to take advantage of the organometallic material's easy dispensability while providing the option to convert to the functional TiO_2 material that is often used in photocatalytic, semiconductor and biomedical applications[1]. Second, the Ti-based organometallic material had steric resemblances to other organometallics with metals other than titanium – theoretically it could be feasible to use the same or similar approach to deposit other metal oxides in such a fashion. For example, Willis et al have developed methods of using metal acetylacetonates as the basis for metal oxides via solvothermal synthesis[2]. Sol-gel approaches were the preferred method as they could be performed at ambient temperatures and without the need for complicated or expensive equipment[3].

The Fe-doped silver-titanium nanoparticles provided another possible functional ink. In this case, they had potential in photocatalytic operations, specifically visible-light photocatalysis. Their advantages lay in their stability and increased shelf-life[4].

Titanium dioxide nanotubes were pursued for their effectiveness in photocatalytic processes[3,5]. A surfactant-based approach was attempted in order to make a more stable suspension of TiO_2 nanotubes for ink deposition. The surfactant approach was based on the possibility of exploiting surface chemistry to induce controlled, reversible, structural changes to the TiO_2 nanotubes, greatly affecting their photocatalytic functionality[6].

2. Experimental Procedure

The Optomec Maskless Mesoscale Materials Deposition® (M3D) (Optomec, Inc., Albuquerque, NM) system and the Sono-tek Ultrasonic Spray deposition systems (Sono-tek Corporation, Milton, NY) were used for the tests. These instruments were housed in the PEARL (Printed Electronics Applied Research Laboratory), located at the South Dakota School of Mines and Technology. In addition, PEARL's Zeiss Microscope viewer and Scanning Electron Microscope (SEM) were used to characterize the materials.

The solutions were deposited in ambient conditions onto a Kapton® (DuPont, Wilmington, DE) polyimide surface. No laser curing or subsequent heat-treatment was conducted on the samples. The samples were atomized prior to deposition. A detailed explanation of the various syntheses follows.

2.1 Titanium Precursor Inks

Using a sol-gel process as the inspiration for the TiO_2 precursor ink[7], the following synthesis was attempted (this will be subsequently called TiO_2 precursor ink 1): Add 0.62 g PVP (polyvinylpyrrolidone, MW ~55,000 Da, Sigma-Aldrich) to 16 mL EtOH (Ethanol, Denatured, Reagent Grade, Sigma-Aldrich). Next, add 12.5 g titanium (IV) oxyacetylacetonate (Sigma-Aldrich), followed by an additional 24 mL EtOH to homogenize the solution. Mix the entire solution at 300 RPM for 12 hours at room temperature. A second form of the precursor ink was attempted, using this synthesis (subsequently called TiO_2 precursor ink 2): Add 5 mL of titanium (IV) isopropoxide (TTIP, Sigma-Aldrich) to 125 mL toluene (Sigma-Aldrich). Add 1.5 g PEG (polyethylene glycol) to assist in material dispersal, and mix the entire solution at 300 RPM, 100 °C, for 1 day. A third form of titanium precursor used the titanium (IV) isopropoxide solution as-is (subsequently called TiO_2 precursor ink 3).

2.2 Iron-doped Silver-titanium Core-shell Nanoparticles

Using a sol-gel process[4], the following was synthesized: Add 3 mL of hydrazine solution (Sigma-Aldrich) to 120 mL of 1 mM cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich) aqueous solution. Stir mixture for 1 minute at room temperature. Add 3 mL of 50 mM aqueous silver nitrate ($AgNO_3$, Sigma-Aldrich). The solution should turn a dark brown, similar to coffee. Next, stir for 10 minutes to ensure completion of the redox reaction. Then, add varying amounts of titanium (IV) isopropoxide to the mixture; in this case, 20 mL of a 1 mM TTIP solution in ethanol (reagent grade, Sigma-Aldrich) was added. Stir vigorously for 10 minutes at room temperature. Finally, add 0.00484 g of iron (III) nitrate ($Fe(NO_3)_3$, Sigma-Aldrich) to the mixture to introduce iron into the nanoparticle solution, and stir vigorously for 10 minutes at room temperature.

2.3 TiO_2 Nanotubes in a Surfactant Solution

This also used a reported nanotube synthesis[3], slightly modified to take advantage of surfactant-based solutions. The synthesis was as follows: Add 1 g of TiO_2 nanopowder (99.9%, ~25 nm, Sigma-Aldrich) to a 10 M aqueous sodium hydroxide solution, and heat the solution at 110 °C for at least one day. Filter the TiO_2 nanotubes and mix 1.28 g into an aqueous solution of 10 mL H_2O and 0.3 mL Surfynol® (CT-136) dispersant. Add a few drops of Surfynol® defoamer as necessary in order to mitigate excess foaming. Shake mixture vigorously for at least three minutes to maximize the surfactant's effectiveness.

3. Results and Discussion

Table 1 compares the various inks and their performance in the Optomec M3D® system and the Sonotek system. Notable was the rate of phase separation in some of the systems, most particularly the Fe-Ag-Ti nanoparticles.

The Ti precursor inks experienced rapid hydrolysis rates, in which the TTIP hydrolyzed quickly in the presence of moisture in the air, forming the desired TiO_2 and organic byproducts. However, the TiO_2 thus precipitated, and because of the rapid rate of reaction, the precursor ink would often clog the system as it was exposed to moisture within the deposition tubes; this resulted in no deposition, as shown in Table 1. This was mitigated by using organic solvents.

Table 1. Comparison of Ink Performance on Selected Systems (Kapton Polyimide Substrate).

Functional Ink	Optomec M3D system (Time until phase separation, consistency of deposition)	Sonotek System
TiO_2 precursor ink 1	5 minutes, inconsistent	N/A
TiO_2 precursor ink 2	11 minutes, inconsistent	N/A
TiO_2 precursor ink 3	35 minutes consistent	N/A (hydrolyzed in system
Iron-doped Ag-TiO_2 nanoparticles	N/A	3 minutes, inconsistent
TiO_2 nanotubes in Surfynol CT-136	<30 seconds, inconsistent	N/A

In the case of the Fe-Ag-Ti nanoparticles, the combined ethanol/aqueous solvent may have been responsible for facilitating a rapid phase separation. This is evidenced by the nanoparticle ink's performance on the M3D® system, where the phase separation was so rapid that it clogged the system almost immediately, resulting in no deposition; this differed from the issues that the Ti precursor inks experienced.

The most effective of the precursor materials was the ink 3, which used the TTIP in its original organic solution. Table 1 shows that ink 3 had the longest uninterrupted deposition period (35 minutes), and a qualitative analysis showed a significantly more consistent deposition pattern than the other Ti precursors. Figure 1 shows the deposition test shapes sampled. Since multiple passes were made in Figure 1, a qualitative analysis indicates that consistency and continuity in the deposition path can be maximized with increasing the number of passes, even if the individual passes occasionally suffer from inconsistency. As shown in Figure 2, the material showed considerable cracking in the material surface, possibly caused by stresses induced in lower layers as ambient moisture seeped into the ink deposition. Despite this, qualitative results demonstrated that the material adhered very well to the polyimide surface.

Based on the performance of the Ti precursor inks as indicated in Table 1, controlling the rate of hydrolysis will be of importance. One method to do this would be to control the level of interaction with moisture by depositing the material in a vacuum; however, depositing the precursor in a vacuum may introduce new issues that did not exist with ambient atmospheric deposition. The alternative is to control the rate of hydrolysis directly; to this end, Dunuwila et al have devised promising methods of controlling the rates of hydrolysis in Titanium (IV) Isopropoxide8, which will be investigated in the future as a possible solution.
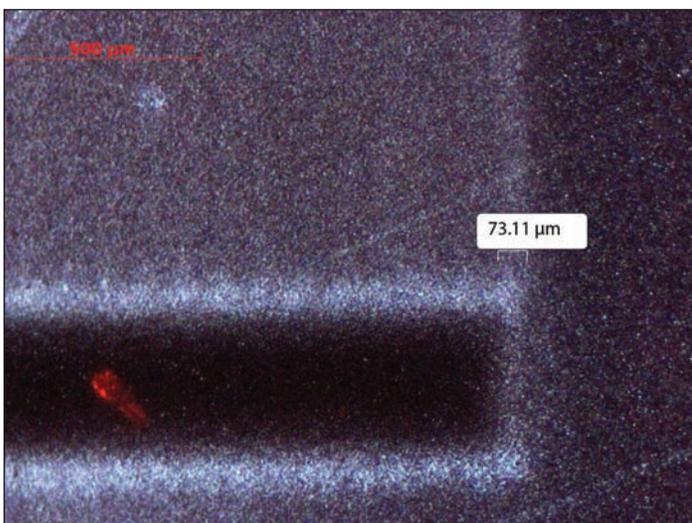
Figure 1. Section of test sample deposition of precursor ink 3 on Kapton® substrate, 133X magnification. Note faint demarcations between depositions.
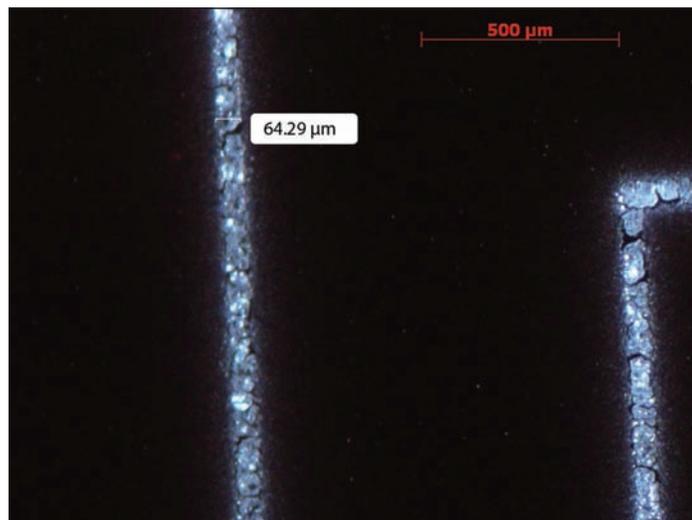
Figure 2. Deposition of precursor ink 3 on Kapton® substrate, 134X magnification. Note significant cracking on surface of deposition.

The iron-doped silver-titanium nanoparticles experienced significant phase separation. This may be attributed to issues with the ethanol having trouble atomizing in the solution. A solution to this problem is to use a surfactant-based approach and changing the solvent to accomplish two goals: improve the suspension of the nanoparticles,

and improve the atomization process. SEM images, as in Figures 3 and 4, revealed a breakdown in the spherical structure of the particles, although this may be attributed to the SEM charging the conductive nanoparticles.
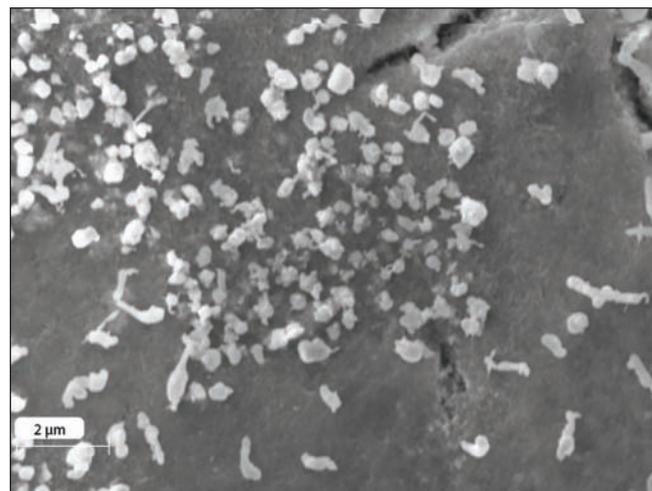
Figure 3. SEM image of silver-titanium-iron nanoparticles at 19,200X magnification.
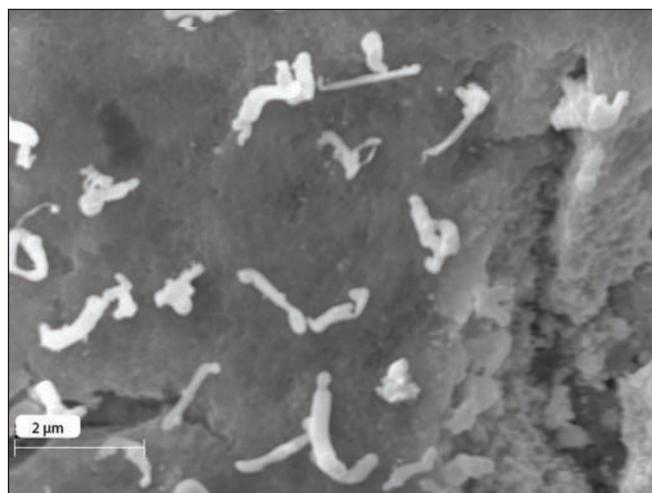
Figure 4. SEM image of silver-titanium-iron nanoparticles at 26,870X magnification.

With the titanium nanotubes, the same issue of rapid phase separation occurred as with the silver nanoparticles, and thus the ink development has experienced considerable setbacks. Most notable was the nanotubes' tendency to rapidly precipitate due to their size. In addition, extended periods of exposure to NaOH caused larger nanotubes to form on the order of microns in diameter as shown in Figures 5 and 6. It is possible that multi-walled nanotubes were being formed in the presence of the NaOH solution, due to the curling induced by the deprotonated environment[6,9]. Several approaches are being considered to resolve this issue, including the use of surfactants optimized for metal oxides (specifically Surfynol CT-324) and using mechanical methods to prevent particle agglomeration (additional ultrasonication, etc.).
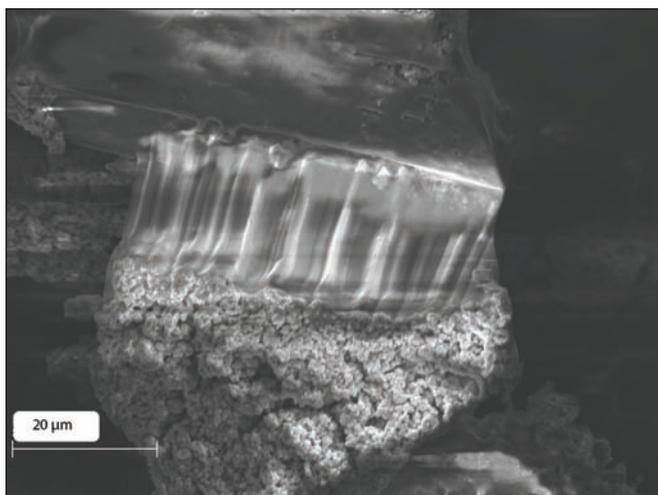
Figure 5. SEM image of TiO_2 nanotubes, 2990X magnification. Note size of TiO_2 nanotube diameters (~2 micrometers).
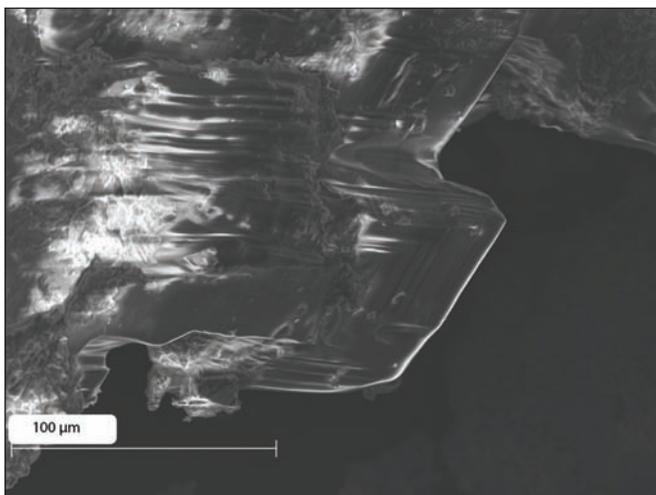

Figure 6. SEM image of array of TiO_2 nanotubes, 1100X magnification.

4. Conclusion

Attempts at deposition of the above materials indicate that problems with phase-separation and rapid hydrolysis must be addressed before the inks can be viable. In addition, surfactant-based approaches will be further investigated to see if they can help significantly improve the viability of the inks. Issues to consider in future work include controlling the rate of hydrolysis and phase separation, to the point where the material will retain its consistency until the actual deposition. Furthermore, methods of curing the depositions to increase their functionality will be investigated.

Acknowledgements

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About the Author

Mitchell Rodriguez is a senior at the South Dakota School of Mines and Technology. He is pursuing a Bachelor dual-major degree in Mechanical Engineering and Materials & Metallurgical Engineering, and will graduate in the spring of 2010. He conducted research through the EPSCoR project for three summer internships. He enjoys reading, swimming and playing his electric guitar when not immersed in work.