Fabrication of Micromechanical Structures of Titania and Titanium with Electrophoretic Deposition

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SUMMARY

This paper describes the fabrication of thick films of titanium and oxides of titanium (i.e., titania) for micromachined structures. In many applications, such as high strength-to-weight ratio and biocompatibility, it is desirable to deposit films of these materials many tens of microns in thickness. However, typical deposition approaches to these materials, such as sputtering and evaporation, are limited in the ultimate thickness that can be achieved, while unfavorable electrochemical properties make them difficult to electrodeposit. This paper describes the fabrication of micromechanical structures of these materials using electrophoretic deposition. Blanket deposition as well as deposition into patterned molds has been achieved with final film thicknesses ranging from 10-200 microns.

Keywords: titanium, titania, electrophoretic, fabrication.

INTRODUCTION

Microstructures fabricated from titanium and titanium dioxide (titania) have a variety of valuable and important characteristics, including extremely high modulus-to-density ratio and the possibility of fabricating biocompatible structures. However, fabrication using these materials is typically limited, in that the thickness of films achievable using sputtering and evaporation techniques is small (typically 0.5-1 micron). Thicker metallic films can be deposited by electrodeposition; however, due to the electrochemical properties of titanium, it cannot be easily electrodeposited from conventional solvents. In this paper, we describe deposition methods for these films based on the technique of electrophoretic deposition, and describe fabrication methodologies to achieve patterned deposition of films of titanium and titania many tens of microns in thickness.

ELECTROPHORETIC DEPOSITION

Electrophoretic deposition (EPD) is a well-known processing technique for the deposition of films and coatings, and has been extensively used for fabrication of coatings in ceramics production [1]. EPD is a combination of electrophoresis and deposition, in which a particle film is deposited onto an electrode. In this colloidal process, charged particles are moved in a fluid due to an electric dc field to an oppositely-charged electrode, where they coagulate into a dense film. This principle is illustrated in Figure 1. In an engineering sense, this deposition method is similar to electroplating, except that a colloidal suspension of particles as opposed to an ionic solution is the 'electrolyte'. As with standard electroplating, deposition occurs on an electrode deposited onto a substrate. If the substrate electrode is patterned or 'masked', by use, e.g., of a deposited polymer mold, deposition into patterns can be achieved.

Hamaker [2] reported that there is no reaction of either the cathode or the anode with the particles involved. The electrodes only provide the electric field to move the charged particles in the fluid. In addition, the electrodes presumably act as sources and sinks of electrons. It is most likely that the positively charged particles and the negatively charged ions of the solution are the carriers of the current [2].
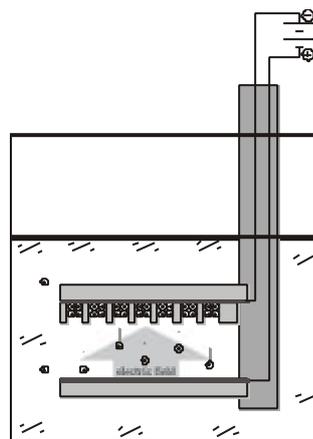

Fig. 1: *Principle of the EPD process. Under the influence of an electric field, colloidally-dispersed particles deposit onto a charged electrode.*

To obtain a satisfactory structure with EPD, the following process steps are required: (1) creation of a stable solution; (2) application of an appropriate electric field; (3) drying of the deposited film; and (4) sintering in a suitable atmosphere to anneal and densify the film. The application of the electric field in appropriate configurations is well-known from MEMS-based electrodeposition; therefore, only points (1), (3), and (4) will be discussed in detail below.

EPD from aqueous solutions is used commercially for shaping of clay based materials and in the production of vitreous enamel coatings. Even though aqueous solutions have been more frequently investigated than non-aqueous media, they have some disadvantages. One disadvantage is that water hydrolyzes at applied voltages above a few volts, thereby limiting the range of deposition conditions and potentially introducing gas bubbles onto the electrode at higher voltages. Another potential problem is corrosion of the anode. Non-aqueous solvents offer the possibility of depositing powders that react with water, such as nitrides, carbides, and superconducting ceramic powders. Furthermore, ceramic powders often develop larger electrostatic potentials when dispersed in organic solvents rather than in water, and the resulting repulsion between particles tends to stabilize dispersions from flocculation, and to reduce sediment volumes. Finally, non-aqueous solutions offer the possibility of using EPD to deposit otherwise readily-oxidizable metals, such as titanium. Disadvantages of organic liquids can be toxicity, safety aspects, costs, and the relatively low dielectric constants, which lead to higher deposition voltages [1]. In the work to be discussed here, deposition from organic alcohols is employed.

The as-deposited EPD material is porous and contains liquid. The drying process is a very important operation prior to firing. If the drying process is not carefully controlled, stresses caused by differential shrinkage or gas pressure may cause defects in the deposited layers.

Factors that determine the obtained layer density and internal stress or cracks are [3]: the solvent that is used; the drying time and rate; the drying method; the particle size, uniformity and shape; and any additives to the solution. A liquid concentration gradient, a non-uniform film or coating, particle orientation, or binder migration (which produce a non-uniform surface permeability), and any nonuniformities in the circulation or temperature of drying air, as well as a mechanical restraint of shrinkage, may cause differential shrinkage and thereby stress in the surface. Cracks or warping may result of this stress.

Both uniform product deposition and uniform drying are required to obtain unwarped products.

The last step in the EPD process is firing. Firing itself consists of three steps: reactions preliminary to sintering, which include organic burnout and elimination of gaseous products of decomposition and oxidation; sintering and consolidation of the product; and cooling, which may include thermal and chemical annealing. In many cases, the firing step can be used to also burn off any molding material used to form patterned ceramic microstructures.

FABRICATION

Substrates

The substrates that were used in this study were 99.5% alumina ceramic, 31x15x1 mm^3 in size. The grain size is approximately 1 μm. Electrodes were deposited onto the surface of the ceramic substrate using an e-beam evaporator and a DC sputterer (the latter only for substrates with steps). Various electrode combinations of titanium, nickel, and platinum, approximately 300nm in total thickness, were employed. Electrodes were used either for (1) blanket EPD; (2) were patterned prior to EPD; or (3) were covered with patterned SU-8 epoxy (Microchem, Inc.) to allow deposition into epoxy wells.

EPD solutions

Rutile and anatase are two stable phases of titanium dioxide particles, and EPD could be performed for either phase. For EPD of rutile titania, the solution was mixed from ethanol (100%, anhydrous), titanium dioxide particles (99.8%, rutile phase, 0.9-1.6μm particle size, Alfa Aesar) and anhydrous iodine beads (99.999%, H_2O<100ppm, Aldrich Chemicals). It was found that the highest stability could be achieved at a composition of ethanol with 1.8 wt% titanium dioxide particles and 0.189 wt% iodine. For EPD of anatase titania, the stable colloidal suspension consisted of absolute ethanol with 0.6wt% titanium dioxide powder (anatase, 99.9%, 32nm APS powder, Alfa Aesar) and 3.36×10^{-2}wt% iodine. Finally, for EPD of titanium, a stable solution was found to be at a composition of the solution of ethanol with 8.31wt% titanium particles (93% (Assay), packaged in 30% water by weight, average particle diameter 1.6μm, Alfa Aesar) and 0.168wt% iodine. Note that the titanium films so produced will likely have incorporated oxygen, which may be able to be removed in a subsequent annealing step in a reducing atmosphere.

RESULTS

Blanket deposition of titania on substrates

The blanket coating of substrate surfaces was investigated. Figure 2 shows a photograph of a substrate after deposition. The electrode on the sample was Ti/Cu/Pt with the thicknesses of 30, 300, and 30nm respectively. In the area of no deposition (the 'scar' in the middle of the substrate) there was no electrode because the sample holder in the e-beam evaporator hid the sample. The deposition time was 5 minutes at a constant current of 1.7mA. After deposition, the sample was dried in an oven at 135°C for 10 minutes and fired in ambient atmosphere. The firing profile was 10°C/min to 1250°C. That temperature was held for 1h, and was finally ramped down to room temperature at 10°C/min. Figure 3 shows the microstructure of the deposited surface coating after firing. It can be seen that the layer is very dense and many particles merged to build larger grains. Typical final film thicknesses on the order of 50 micrometers were achieved. Changing the electrode material to titanium did not change the final layer but increased the necessary deposition current to 3mA. Exchanging copper with nickel led to poor adhesion.

Deposition of titania into patterned molds

To investigate deposition into molds, an SU-8 epoxy mold was fabricated onto the electrode using standard techniques. The particles were deposited into the molds with the EPD process. The sample was exposed to a current density of 0.04mA/mm² for 10 minutes. The sample was then dried and fired in ambient atmosphere. An SEM photograph of a mold after deposition can be seen in Figure 4. The deposit is relatively flat in the middle and irregular growth can be seen at the interface to the epoxy mold. The sample was then fired. The firing profile used a ramp rate of 5°C/min to 1300°C, that temperature was held for 1h, and finally ramped down to room temperature at 5°C/min. Figure 5 shows an SEM photograph of a single fired bar. The height of the bar was measured in the SEM to be 160-190 µm. As the deposited layer is very thick and nonuniform in height, warping of the sample is evident.

Another approach to structured deposition is to eliminate the mold and deposit directly onto a patterned electrode. An electrode patterned into bars 400-1400 microns in width was exposed to EPD for 5 minutes with a current density of $0.04mA/mm^2$. After the deposition, the sample was dried at ambient atmosphere for 20 minutes. After drying, the sample was fired in a pure oxygen atmosphere with the following heating schedule: 4°C/min to 1200°C, hold for 2h, cool down with 4°C/min.

The firing process did not change the lateral dimensions of the deposited layer significantly. After firing, the thickness of the deposited material was approximately 200 micrometers. Figure 6 shows a photomicrograph of the deposited pattern after firing.

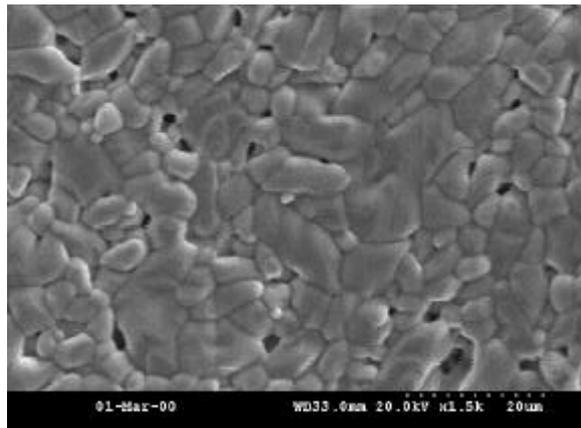**Fig. 2**: *Photograph of a ceramic substrate after deposition of titania.*

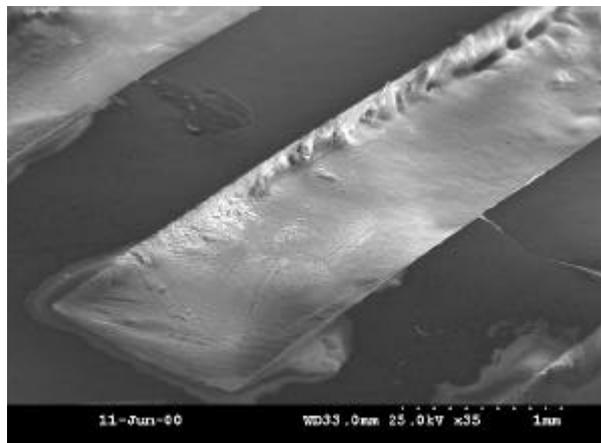**Fig. 3:** *SEM photograph of the surface of Figure 1 after firing.*

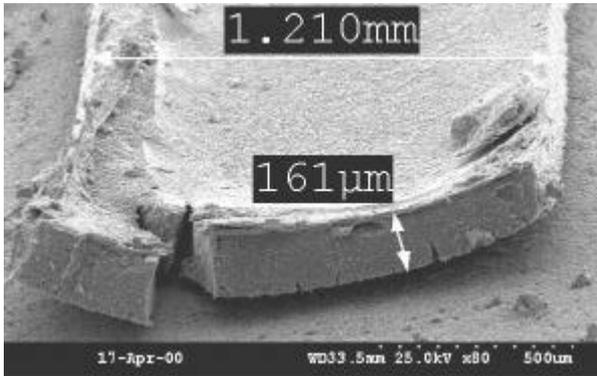**Fig 4:** *SEM of a filled mold after TiO₂ deposition.*

Fig 5: *SEM photograph of a titania bar deposited into an epoxy mold after firing. Firing has simultaneously removed the mold.*

Fig 6: *Photomicrograph of titania deposition onto patterned electrodes after firing. The thickness of the deposited film is in excess of 100-200 microns. Linewidths range from 400 to 1400 microns.*

Blanket deposition of titanium on substrates

To test the EPD of titanium metal, an alumina ceramic substrate was coated with a 300nm titanium electrode. The deposition was carried out from the titanium EPD solution described above for 5 minutes at a constant current of 0.032mA/mm². A consistent and uniform layer was deposited, as can be seen in Figure 7. The sample was then fired in a pure argon atmosphere using a ramp of 3°C/min to 1300°C. The temperature was held for 1 hour and was than ramped down to room temperature at 3°C/min. The result can be seen in Figure 7. Thickness variation was evident in the sample, and the thicknesses in various regions (labeled 1-3 in Figure 7) were measured using a microscope. The variation in height and the measured sheet resistivity can be seen in Table I. The electrical resistance of bulk titanium is in the range of 4.2×10^{-5} to $7 \times 10^{-5} \Omega$cm. The black, even area ❶ comes very close to this range, while areas ❷ and ❸ are far from the values for the bulk material. That indicated that the layer has electrical properties that can approach those of bulk titanium if it is properly deposited and
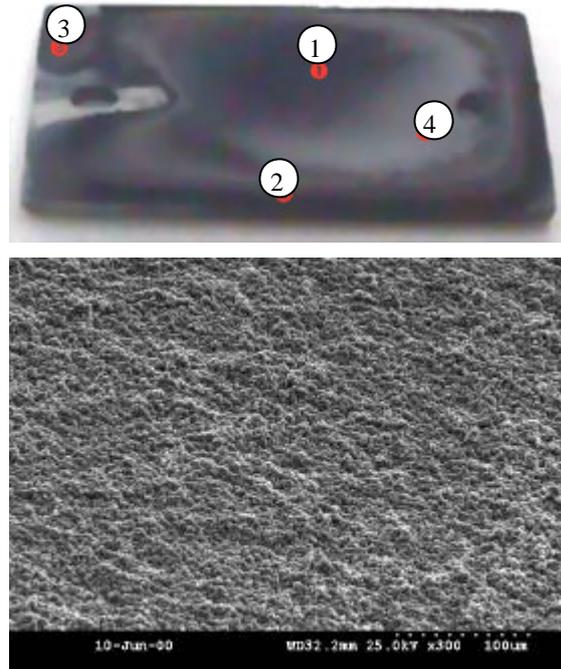

Fig. 7: *Titanium surface coating after firing. Top: optical micrograph; bottom, SEM of area* ❶

fired. The surface roughness is a few micrometers, as can be seen in the SEM of Figure 7. Note that the surface roughness is on the order of the particle size in the original EPD solution.

Table I. Sheet resistivity of deposited titanium films in the various areas shown in Figure 7.

area	thickness of the layer μm	sheet resistivity $m\Omega$	resistivity Ωcm
❶	22	19	4.18E-05
❷	64	103	6.59E-04
❸	11	1120	1.23E-03
❹	4	29	1.16E-05

CONCLUSIONS

Electrophoretic deposition of titanium and titania into patterned molds and onto structured electrodes has been demonstrated. This approach may be a desirable one for the deposition of relatively thick films of these materials in many micromachined systems.

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