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Microplasmas for direct, substrate-independent deposition of nanostructured metal oxides

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A general, substrate-independent method for plasma deposition of nanostructured, crystalline metal oxides is presented. The technique uses a flow-through, micro-hollow cathode plasma discharge (supersonic microplasma jet) with a “remote” ring anode to deliver a highly directed flux of growth species to the substrate. A diverse range of nanostructured materials (e.g., CuO, α-Fe2O3, and NiO) can be deposited on any room temperature surface, e.g., conductors, insulators, plastics, fibers, and patterned surfaces, in a conformal fashion. The effects of deposition conditions, substrate type, and patterning on film morphology, nanostructure, and surface coverage are highlighted. The synthesis approach presented herein provides a general and tunable method to deposit a variety of functional and hierarchical metal oxide materials on many different surfaces. High surface area, conversion-type CuO electrodes for Li-ion batteries are demonstrated as a proof-of-concept example.

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The ability to synthesize functional nanoscale materials, as well as to integrate these structures into devices, is fundamental for the development of next-generation micro- and optoelectronic devices, sensors, and energy harvesting and storage technologies.1–4 Realization of nanomaterials and multi-scale systems often requires complicated processing steps that may involve a combination of wet chemistry, physical/chemical vapor deposition, vapor-liquid-solid or molecular beam epitaxy, self- and/or directed assembly, lithography, and etching. In addition, both wet and dry conditions, long processing times, high temperatures, vacuum processing, and templates or catalysts can be required. As such, we continually seek to develop general and tunable methods that can easily and rapidly create nanostructured functional materials. For example, atmospheric pressure plasmas,5,6 plasma sprays,7–9 and microplasmas10–20 have shown much promise toward this goal. Extending and adapting such methods in a generic way to different material systems and deposition situations, as well as understanding how plasma operating conditions affect growth processes, is critical for their implementation.

In this work, we present a general, microplasma-based approach for direct deposition of nanostructured and conformal, crystalline metal oxides (CuO, NiO, and α-Fe2O3) on virtually any substrate (e.g., conductors, insulators, polymers, fibers, and patterns) at room temperature. A supersonic DC microplasma jet is seeded with organometallic precursors under oxidizing conditions to create a directed flux of growth species (e.g., atoms, ions, clusters, and/or nanoparticles) that are subsequently “spray-deposited” onto the surface of interest. A remote, concentric ring anode, instead of the substrate, is used to complete the plasma circuit, allowing deposition on both conducting and insulating surfaces. Herein, we highlight the diverse range of materials that can be realized using microplasma growth and discuss how plasma operation and deposition conditions affect film morphology. High surface area CuO films were tested as conversion reaction anodes for Li-ion battery applications to demonstrate the incorporation of microplasma-deposited films into devices, and the potential of microplasmas to synthesize nanostructured materials for energy applications.

Metal oxide nanostructures were deposited on a variety of different substrates using the microplasma deposition system depicted in Fig. 1. A flow-stabilized, direct-current hollow cathode discharge was used to crack sublimed organometallic precursors into active growth species (e.g., atoms, ions, and clusters), which were directed towards the substrate under supersonic flow conditions. Nickelocene, ferrocene, copper(II) acetylacetonate (Cu(acac)2), and copper(II) hexafluoroacetylacetonate hydrate (Cu(hfac)2 xH2O) (Strem Chemicals Inc.) were sublimed and fed with 100–300 sccm Ar to the plasma jet cathode (stainless steel capillary, ID = 500 μm) that was biased with current-regulated, DC high voltage (~10 mA, 300–800 V). A macor-insulated stainless steel ring near the capillary exit served as the anode to complete the plasma circuit. Oxygen (50–100 sccm) was introduced into the cathode gas feed or chamber background, the latter being maintained at 10–50 Torr. The substrate stage, 8–12 mm downstream from the capillary exit, was static or raster-scanned in a serpentine pattern at a rate of 2–10 μm/s during growth. Deposition rates varied for different materials, but generally fell in the 50–100 nm/min range, measured directly beneath...
the jet centerline. Substrates were conducting (\(<0.001\ \Omega\ \text{cm}\)) and insulating (\(>2000\ \Omega\ \text{cm}\)) Si, glass coverslips, 300 nm ITO on glass, 50 \(\mu\)m Kapton polyimide film, 125 \(\mu\)m polished stainless steel, carbon paper, and fiberglass cloth. Deposition on patterned Si, i.e., micropillars created using colloidal lithography and reactive ion etching (see Ref. 21 for details), was also considered in order to evaluate if the deposited oxide films were conformal.

Crystallinity and phase of the deposited oxide coatings were analyzed via \(\theta-2\theta\) XRD (with \(-4^\circ\) offset to suppress Si substrate peaks) using Cu K\(\alpha\) radiation on a PANalytical Empyrean diffractometer; high resolution micrographs and energy dispersive x-ray (EDX) spectra were taken on an FEI XL40 SEM and an FEI Tecnai G2 F20 S-Twin TEM using lacey carbon grids. X-ray photoelectron spectroscopy (XPS) analysis (see supplementary material22) also showed Cu\(^{2+}\) with characteristic CuO shakeup satellites, and no indication of Cu\(^0\). Scherrer analysis of the (111) and (111) reflections from the CuO nanowire sample estimates crystallite size at \(~11\ \text{nm}\). The early stages of CuO growth were investigated by directing an Ar/Cu(hfac)\(_2\) jet onto a lacey carbon TEM grid for 1 min [Fig. 3(e)]. Although the plasma jet flow distorted the fragile lacey carbon grid, a conformal coating of small (<5 nm), seed-like CuO crystal growths with facets can be seen. The corresponding selected area electron diffraction (SAED) pattern [panel (f), inset] for this sample indicates that the seeds are indeed crystalline CuO, with reflections corresponding to the monoclinic tenorite phase.
The microplasma deposition technique can also be easily extended to other oxide systems, such as NiO and $\alpha$-Fe$_2$O$_3$, and for conformal deposition, as shown in Fig. 4. Similar plasma operating parameters (20 Torr, 8.5 mA, Ar:O$_2$ = 8:1 with O$_2$ in the jet) and static substrate were used to deposit both oxides on silicon micropillars at room temperature. Oxide coverage was reasonably conformal, with growth at the tops of pillars being favored due to shadowing effects. The observed crystal habits for each oxide were consistent with the bunsenite (rock-salt) phase of NiO and the hematite (rhombohedral) phase of $\alpha$-Fe$_2$O$_3$. Scherrer analysis of the NiO (200) and Fe$_2$O$_3$ (104)/(110) reflections gave crystallite sizes of 20 and 23 nm, respectively. XPS of the films (supplementary material) additionally showed Fe$^{3+}$ and Ni$^{2+}$ chemical environments, in agreement with the Fe$_2$O$_3$ and NiO phases seen by XRD.

Finally, nanostructured CuO films were evaluated as conversion electrodes for Li-ion batteries. CuO directly spray-deposited onto a copper foil current collector was assembled in a Swagelok cell against a Li metal anode with filter paper separator and cycled at a rate of C/20. As can be seen in Fig. 5, the microplasma-deposited electrode exhibited high specific capacity and good cyclability (~650 mA h/g over several charge-discharge cycles). The large and irreversible capacity loss after the first discharge-charge cycle is characteristic of CuO and other transition metal oxide conversion materials. This loss is attributed to several factors including the incomplete conversion of Cu into Cu$_2$O instead of CuO during charge, cracking due to large volume expansion that could compromise electrical contact, and the formation of a solid electrolyte interphase (SEI). Despite the irreversible capacity loss in the first cycle, a capacity of about 650 mA h/g was retained over several cycles and is similar to the capacities reported for CuO-based electrodes synthesized by traditional chemical methods. The microplasma-deposited films have the added benefit in this application of not requiring conductive carbon additives or polymer binders for electrode preparation, which can constitute 15% of the electrode film’s mass. This preliminary result demonstrates both the ease of integrating microplasma-grown materials into devices with minimal processing as well as the viability of microplasma deposition to synthesize materials for energy applications.

In this work, we demonstrated a simple, microplasma-based approach for direct, low temperature deposition of nanostructured metal oxides on a variety of substrates ranging from conductors to insulators, and polymer films to
fibers. The films were highly crystalline and conformal, and raster scanning the substrate allowed deposition over larger areas with a single microplasma jet. Overall, we believe that microplasmas have great potential in materials processing, and deposition methods can be extended to a wide range of functional materials and hybrid structures for use in micro- and optoelectronics, sensing, and energy applications.

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FIG. 5. Discharge-charge profiles for microplasma-deposited CuO on Cu foil, used as a Li-ion battery anode. Testing configuration was a Swagelok cell operating at C/20 with 1M LiPF6 in 1:1 v/v ethylene carbonate:dimethyl carbonate electrolyte and Li-metal cathode. (Inset) SEM image of the CuO film.

22See supplementary material at http://dx.doi.org/10.1063/1.4959564 for XPS results.