Multi-layer Micro-structured Films

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Abstract
Multi-layered films deposited in micro-structured patterns exhibit unique structural and functional properties dependent upon the materials, pattern designs, and layer thickness. By incorporating a lattice of one material with line dimensions of 100nm between layers of similar or dissimilar materials the mechanical and optical properties of the films are modified to exhibit enhanced responses including stress balancing, directional reflectance, scattering, absorption, and interference that can be used for visual enhancement, shielding, or camouflage. Each layer in these multi-layered films range from 100 to 1000nm and requires precise control of rate, angle of deposition, stress, and density. Using ion beam assisted deposition, stable reproducible micro-structured single layers are deposited and combined with continuous layers in multi-layer stacks.

Introduction
Material multi-functionality is a key component in the development of smaller, lighter and more powerful devices for application in a broad range of frequency dependent environments [1]. One way to achieve this multi-functionality is to incorporate structure into a thin film device that has a frequency specific response for the material and a separate response to structure (i.e. visual transparency and microwave reflection). In particular, the pursuit of superior properties by synthesizing low dimensional architectures in engineered nanocomposites has led to a new class of materials called metamaterials that are being investigated as frequency selective surfaces, photonic bandgap structures, and negative index materials [2]. While this new class of materials and applications have been theoretically postulated since the 1960s [3-6], it has only been since 2000 that patterning processes such as lithography [7-9], nanoparticle assembly [10] and nanofabrication [11] have progressed to the point of experimental demonstration. Commercial products and industrial processes to make these unique structures are under development at national laboratories [12], start-up companies [13] and large technology companies (IBM, Intel,) [14,15]. Structures have been built in the microwave and infrared regime but the immediate challenge is to fabricate composite structures that possess spectral gaps at frequencies up to the optical region [16]. In this paper, the theoretical principles, potential commercial fabrication processes, and commercial opportunities will be reviewed and the experimental approaches under development at Southwest Research Institute® are presented.

Experimental
Multi-layer optical thin film deposition was carried out on a multifunctional vacuum coater (5.0 X 10^-7 Torr) utilizing a multi-pocket electron beam evaporation source. Four substrates six inches in diameter were mounted on a double rotation planetary system with a source to substrate distance of twelve inches. Film thickness was monitored and controlled with a quartz crystal and an optical monitor system. Films of aluminum, silver, silica, and titania, were deposited in a thickness range of 100 to 1000nm.
Discussion
Historically, patterning of products coated using physical vapor deposition (PVD) has been achieved by pre or post chemical treatment outside of the vacuum environment [17]. New techniques to pattern in-situ by printing a layer to promote or discourage adhesion at the substrate surface are being adopted on a commercial scale. The line spacing and thickness achievable by these techniques is on the order of tens of microns [18]. While the present resolution has application in macro and microscopic enhancement of roll coated products for packaging, security devices, and flexible circuit markets, an order of magnitude reduction in line resolution is anticipated to open several opportunities in the display, defense and biomedical fields [19].

Virtually all roll coated optical thin film products are based on the fundamental principle of the wave nature of light and the superposition of coherent waves to produce interference. Products based on interference are used in everyday products from currency to fiber optics to displays [20]. These optical designs are well understood and can be regularly manufactured in multi-layer constructs to serve a singular function within the end product. The inclusion of sub-wavelength structure within these films has been considered a defect, contamination, or failure due to the discrepancies between the optical performance based on classical optical thin film models and that observed when sub-wavelength structure is included [21].

As nanotechnology has advanced and new structures have become viable, the principles of reflection, refraction, diffraction and interference cannot be used for sub-wavelength structures as the equations describing conventional optical behavior do not fully cover the resultant phenomena because quantum mechanical effects come into play. The possibility of exploiting patterns arising through the use of vicinal surfaces represents an alternative, promising approach to obtaining one-dimensional arrays of atoms and molecules. Combining contiguous thin films with nanopatterned layers as nanostructured composites introduces nonlinear optical properties such as massive signal enhancement, light generation and waveguiding. Integration of a patterned layer into a multilayer system provides the opportunity to get multi-functionality into a single thin film device.

Much like macrostructures, the two general approaches to achieve nanostructures are either additive or subtractive. The following table lists areas under development.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Feature Size (nm)</th>
<th>Area (inches²)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Additive</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ink jet</td>
<td>30,000</td>
<td>60</td>
<td>flexibility</td>
<td>fluid dynamics</td>
</tr>
<tr>
<td>Flexo</td>
<td>50,000</td>
<td>unlimited</td>
<td>large area</td>
<td>resolution</td>
</tr>
<tr>
<td>Masking</td>
<td>1000</td>
<td>unlimited</td>
<td>simplistic</td>
<td>variation</td>
</tr>
<tr>
<td>Xerography</td>
<td>100</td>
<td>6.5</td>
<td>scalability</td>
<td>process control</td>
</tr>
<tr>
<td>MBE</td>
<td>40</td>
<td>1</td>
<td>atomistic</td>
<td>slow</td>
</tr>
<tr>
<td><strong>Subtractive</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laser Ablation</td>
<td>70</td>
<td>12</td>
<td>single step</td>
<td>surface damage</td>
</tr>
<tr>
<td>Lithography</td>
<td>15</td>
<td>unlimited</td>
<td>resolution</td>
<td># of steps</td>
</tr>
<tr>
<td>Maskless Etch</td>
<td>40</td>
<td>6</td>
<td>dry</td>
<td>small area</td>
</tr>
</tbody>
</table>
Some of the more advanced additive processes include flexographic and inkjet printing of nanoparticles, nanoxerography, deposition masking and molecular beam epitaxy. The advantages of an additive process are fewer process steps, improved material utilization and a more direct route to a multi-layer system. The disadvantages include lack of speed, line width and spacing, and process instabilities. Subtractive approaches such as lithography, ablation and dry etching have the advantages of atomic level resolution, demonstrated roll to roll processes, and a wide material portfolio. The drawbacks of a subtractive process are the additional process steps (often 3-6 more than an additive process), contamination from the removal processes and poor material utilization. There is no clear cut technology favourite in the race to produce nanopatterned films particularly when large area high speed roll coaters are considered.

In the IC world, top-down nanofabrication — heir to microfabrication, using subtractive and additive processes to build devices on a finer and finer scale — appears to be the path of most progress. In research on quantum devices, biological applications, and sensors bottom-up nanochemistry (molecular engineering) is showing progress. The synergy between nanofabrication and nanochemistry appears to be the most fruitful research domain for roll coating of the multi-functional films.

Deposition of materials via traditional vacuum methods (evaporation & sputtering) onto a surface that promotes selective adhesion by thermal and optical means is the approach under development. Atoms that hit a surface in a vacuum are either immediately reflected, re-evaporate after residing on the surface or condense. The mobility of an atom on a surface (adatom) depends upon the energy of the atom, the atom/surface interactions, and the energy within the surface. By introducing localized heating or cooling of the substrate two of the adatom mobility properties can be controlled and with adequate confinement structures on the order of nanometer dimensions are achievable. Using the Structure Zone Model (SZM) principles confined to localized areas, films deposited at a thickness below 100nm form a pattern corresponding to the cooling or heating patterns on the substrate. Further pattern enhancement by accentuating the differences between the heated and cooled areas of the patterned film promotes feature resolution.

Multi-layer films with patterned layers between non-patterned layers exhibit individual layer uniformity and conformal deposition onto the preceding layer. While pattern resolution and pattern continuity are not at feature sizes conducive to metamaterial properties further refinement of the patterning features and deposition conditions are under development. Several areas exist for refinement and improvement of the control of the adatom mobility. If PVD processes for applying a thin film to a surface are simply defined as a source, the vapor phase, and a substrate, each of these require further investigation to promote structure within a layer. Alternative deposition methods such as inkjet or co-evaporation of dissimilar materials to better control the energy of the atoms are under development. Vapor phase refinement such as pressure control, introduction of reactive or getter materials, and angle of incidence manipulation to promote structures within the thin film layers are under investigation. Alternative methods to introduce energy into the substrate such as patterned electron emitters, dual beam laser interference and surface bombardment are all achievable using commercially available equipment that is appropriate for metamaterial resolution and for the large area applications of interest to roll coating.
Conclusions

Development of new approaches that allow practical control of material structure and morphology at the nanometer scale is of tremendous importance. There are extensive applications in photonics, electronics and catalysis where the inclusion of structure at dimensions below the optical wavelength of light will introduce order of magnitude improvements in material and device performance. Incorporating these nanostructures within traditional thin film layers provides a platform to achieve multi-functionality for miniaturization. Utilizing the principles of structure zone modeling, patterns of nanometer dimensions have been deposited that offer a simple and robust approach to in-situ fabrication of nanostructured surfaces and thin-films with long range order.

References

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