ENGINEERED BIOMIMICRY: POLYMERIC REPLICATION OF THE
SURFACE OF A COMPOUND EYE OF AN INSECT

A Thesis in
Engineering Science

by
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Abstract

The conformal-evaporated-film-by-rotation (CEFR) technique was modified to improve the uniformity of roughly 800-nm-thick films deposited on nonplanar biological templates and this modified-CEFR technique was implemented in the fabrication of high fidelity nickel dies that may be used to produce multiple replicas by casting or stamping. The CEFR technique was developed to produce high-fidelity replicas of the surfaces of biological specimen. By thermally evaporating a robust inorganic material in high-vacuum conditions while rapidly rotating the sample about the surface normal to a substrate on which a biotemplate is mounted while the substrate is held obliquely with respect to the direction of incident vapor flux, it is possible to produce a coating on a biotemplate that conforms to the surface features of the biotemplate. An inorganic replica can be made by removing the original biotemplate by plasma ashing. It was thought that the CEFR technique may not perform ideally when highly nonplanar biotemplates were to be replicated. To investigate if this was the case a series of common blowfly corneas were coated and their thickness and morphological uniformity evaluated. In an effort to adapt the CEFR technique to use with nonplanar biotemplates rotation about a second axis lying wholly in the substrate plane was introduced. The rotation about this second axis was tailored to produce a more uniform time-averaged vapor flux over the whole sample. Film thickness and morphology were observed for both CEFR and modified-CEFR produced films and compared. The modified-CEFR coating showed half the variation in film thickness over the sample when compared to the CEFR produced coating. It was shown that film structure varied over the surface of CEFR produced coatings while the modified-CEFR produced coating exhibited a uniform film structure over the entire sample.

With the modified-CEFR technique established I set out to produce a die that could be used to produce multiple replicas from a single biotemplate. This was done by a combination of the modified-CEFR technique and nickel electroforming. An approximately 250-nm-thick amorphous nickel film was deposited on an array of blowfly corneas to capture the surface features of the cornea in high fidelity and then a roughly 60-µm-thick structural layer was electroformed onto the thin film layer to give it the structural integrity needed for casting or stamping. The feature resolution of this die was then evaluated and PDMS castings made using the die.
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<td>$\chi_v$</td>
<td>Angle measured between the average vapor flux direction and the flat surface of the platform to which the biotemplate is affixed</td>
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<tr>
<td>$\chi_L$</td>
<td>Angle measured between the average vapor flux direction and the local tangential plane to the surface of the biotemplate</td>
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<tr>
<td>Ge</td>
<td>Germanium</td>
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<tr>
<td>Se</td>
<td>Selenium</td>
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<td>Sb</td>
<td>Antimony</td>
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<tr>
<td>Ge$<em>{28}$Sb$</em>{12}$Se$_{60}$</td>
<td>Schott IG5 chalcogenide glass</td>
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<td>Ni</td>
<td>Nickel</td>
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<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<td>QCM</td>
<td>Quartz Crystal Monitor</td>
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<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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Dedication

This work is dedicated to my friends and family who provide the spontaneous distractions that keep life fresh and exciting.
Chapter 1

Introduction

A brief inspection of any biological specimen will reveal that it possesses a plethora of very complex features and mechanisms that operate rather well together resulting in the condition we call life. From the perspective of an engineer, living organisms are the ultimate machines; they reproduce, self-repair to a certain extent, adapt to changing conditions and demands, and seek out sources of energy. In many cases they have been doing for millions of years what man has only created devices capable of in the last hundred years. Living organisms have been converting sunlight to fuel, flying long distances, diving to the depths of the oceans, and fabricating on the nano-scale far longer than man has walked the earth. Some of mankind’s earliest advancements came from harnessing the capabilities of organisms. The domestication of plants and animals allowed mankind to create permanent settlements. The first cutting tools may have been inspired by, if not made from, the teeth and claws of animals. Mankind rode on the backs of horses to more rapidly cover distances, attached messages to pigeons to rapidly communicate over long distances, and used the noses of domestic dogs to track prey. It is obvious that mankind has been aware of capabilities of other organisms for a long time, and has been directly using or mimicking them.

Although we have drawn from nature greatly, mankind is not without originality in designing
certain devices. Technological advancements such as the steam engine, transistor, and radio among others seem to have developed without biological inspiration. The rise of the physical and chemical sciences in the 17th through 19th centuries layed the ground work for the technological explosions that were witnessed in the 20th century. In this era, mankind’s understanding of science and engineering were the inspiration for new technologies. Integrated circuits brought with them a new domain in which engineers can operate, design, and invent. Nanotechnology essentially rose from the rapid reduction in dimensions of transistors in an integrated circuit.

Mankind’s entry into the realm of nanofabrication has again opened the door for drawing inspiration from nature. Inspection via electron microscopy shows that nearly every insect has one or more remarkable microstructures, the most apparent of which are diffraction gratings that cause many insects to exhibit some degree of iridescent coloration. In many cases the micro- and nano-structures found on biological specimen are spatially complex and detailed to such an extent that analogous structures are nearly impossible to produce by conventional nanofabrication methods. The situation where engineers simultaneously recognize a unique structure, potential applications for that structure, and a method for producing that structure sets the stage for bioinspiration, biomimetics, or bioreplication to take place.

1.1 Background

Bioinspiration, biomimetics and bioreplication are progressions along the same line of thought. That line of thought—engineered biomimicry—is that we can draw from nature when designing new structures and devices. Of the three approaches, bioinspiration is the one most often applied by design engineers: is when inspiration is drawn from a natural structure for its specific functionality, and then a device is fabricated that exhibits a similar functionality. With bioinspiration the goal is to reproduce the function found in nature but not necessarily the structure. An example of bioinspiration is the development of powered flying machines that were inspired by birds in
self-powered flight. Figure 1.1 shows a photograph of the Wright flyer. There are not many components of the flyer with bird-like structures, and this illustrates how the function is being reproduced but with non-avian structures.

Biomimetics is the next step in the progression: engineers attempt to replicate the functionality of a biological structure by approximately reproducing an essential feature of the structure. A terrific example of biomimetics is the approximate structure of Velcro coming from the hooked barbs on a burdock seed. Figure 1.2 shows a photograph of a burdock seed. When an animal brushes against the seed, the hooks attach into the fur of the animal and the seed is carried along until it is either pulled off or drops out of the fur.

The third way in which engineers are able to draw from nature to produce new devices is by bioreplication: the direct replication of a structure found in natural organisms. To date there are no commercial bioreplicated devices on the market but engineers have been able to replicate structures such as insect eyes and butterfly wings. Figure 1.3 shows a photograph of the corneal layer of a blowfly’s eye on the left and a photograph of a nickel replica of the corneal layer on the
Figure 1.2. Photograph of a burdock seed

Figure 1.3. Photograph of the corneal layer of a blowfly’s eye (left) and a nickel replica of the corneal layer (right)

right. This replica was produced, for this thesis by first coating the corneal layer of a blowfly eye with physical vapor evaporation and then plasma ashing away the original eye to leave behind only the metal replica.
1.2 Survey of bioreplication techniques

Bioreplication is in its infancy and the first step is to devise fabrication techniques that can be used to produce replicas of the biological structures of interest. To date, bioreplica fabrication techniques have drawn heavily from semiconductor processing. Techniques such as atomic layer deposition (ALD), physical vapor deposition (PVD), sol-gel, lithography, and focused-ion-beam milling (FIB) have all been used to produce bioreplicas [1, 2, 3, 4, 5]. Several techniques are briefly described here and more detail is given on the PVD method in following sections.

ALD has been used to produce alumina replicas of butterfly wings and the compound eyes of flies. For example, ALD was used to produce a 100-nm-thick alumina coating on a fly eye, and then the biotemplate was removed by pyrolysis. The resulting replica captured features down to the 200-nm features that pattern the surface of the lenslets that the compound eye is made of [5].

Sol-gel techniques have been used to replicate the three-dimensional structure found in the elytra of various beetles. Replication begins by filling the void region of the structure with silica and then etching away the original chitinous structure. Finally, the silica negative is refilled by titania and the silica is removed leaving, only the titania replica. This method is successful in reproducing the photonic bandgap properties of the original structure [6].

Soft lithography techniques have been used to replicate the surface structures found on various plants. The leaves are replicated using a two-step process where first a polymer master is produced and then is filled to make a polymer replica of the original biotemplate [7].

Several groups have also produced moth-eye structures by conventional and imprint lithography by methods more accurately described as biomimetics [8, 9].
1.3 OAD and CEFR

The technique I employ to achieve direct, high-fidelity replication of biological surfaces is a physical-vapor-deposition method dubbed the conformal-evaporated-film-by-rotation (CEFR) technique [4, 10, 11, 12]. This technique is an offshoot of the oblique-angle deposition (OAD) technique. Usually in OAD, a planar substrate is held on a platform at an angle $\chi_v$ with respect to the average direction of a directional vapor flux, as shown in Figure 1.4a, in a vacuum chamber. Under the right conditions, the film deposited on the substrate is an array of parallel columns that are tens of nanometers in diameter and inclined with respect to the substrate by an angle equal or larger than $\chi_v$ [13, 14]. Such a thin film is called a columnar thin film (CTF) [15, 16]. If the platform holding the planar substrate is slowly rotated about a normal axis, the columns formed are like corkscrews, and the deposited film is called a chiral sculptured thin film [15]. If the platform is rotated rapidly during deposition, the corkscrews coalesce into columns tilted normally to the planar substrate [17].
The CEFR technique involves rapid rotation of the platform to which is affixed a nonplanar substrate such as a biotemplate, as shown in Figure 1.4b. In Chapter 2 I will introduce the Modified-CEFR technique that is shown schematically in Figure 1.4c. For bioreplication, a film of thickness $\lesssim 1000$ nm is usually desired.

The array of parallel-upright-nanoscale columns is analogous to a pin toy [15]. When the pin toy is placed on top of an object, the topography of the object is transferred along the pins to the upper surface. The resolution of the reproduction created by the upper side of the pins is determined by the diameter of the pins. The upright columns produced by the CEFR technique constitute a pin-toy replica with pin diameter of tens of nanometer [18]. The small columnar diameter and rapid rotation of the platform allow us to conformally coat many types of nonplanar substrates. To date, the CEFR technique has been successful in reproducing the structures found on: the wings of butterflies [10, 11] and moths, the compound eyes of fruit flies [4] and blowflies [19], and manufactured devices such as an electronic comb resonator [12].

The advantages that the CEFR technique holds over other bioreplication methods are as follows: the sample (biotemplate) remains at nearly ambient temperature during deposition, the deposition rate can be tens of angstroms per second, and the process is entirely physical [13, 14]. Low temperature is critical when working with biological samples, as they can be damaged by high temperatures. A reasonable deposition rate is key in any process that is to be implemented on an industrial scale. As with temperature, the absence of corrosive precursors helps to ensure that the sample is not altered during the deposition process. After separation from the biotemplate, a coating becomes a replica [4, 11].

### 1.4 Outline

A replica may be used as a freestanding optical device. Many potential optical applications for CEFR-produced replicas require them to be very uniform in thickness and structurally robust.
As such, it became pertinent to take a closer look at the uniformity of both thickness and morphology of CEFR-produced coatings. In Chapter 2 I describe how I found these coatings to have poor uniformity in both thickness and film structure, when the biotemplate is significantly nonplanar, which prompted me to modify the CEFR technique to rectify these shortcomings. The resulting modified-CEFR technique resolved these issues with the original CEFR technique. In the following chapter I show how a consideration of the shape of the biotemplate and tailoring the motion of the platform holding the biotemplate can result in coatings with improved uniformity in thickness and morphology.

If bioreplicated structures are ever to find applications, a method of bioreplication that is both sustainable and scalable must be developed. In essence a bioreplication technique that produces many high-fidelity replicas for the sacrifice of a single biotemplate is needed. Immediately what comes to mind is a master replica produced from the biotemplate that can be used to produce many subsequent replicas. The progression of this line of thought leads to the possibility of implementation of techniques such as imprint lithography and nanocasting to biomimetics. The complicated aspects of both of these techniques is the production of the master die. In Chapter 3 I describe a die-making technique that makes use of the modified-CEFR technique and nickel electroforming to produce robust dies that can be used to produce multiple replicas of a blowfly’s cornea.

In Chapter 4 I discuss several failed attempts at evaporating nickel, mounting the blowfly corneas, and removing the replicas from the nickel die. This chapter details techniques that may be deadends and not further pursued.

Chapter 5 concludes this thesis and describes the motivation, achievements, and future of this research. The motivation for this thesis was to develop a bioreplication technique that allows me to produce multiple-high-fidelity replicas of the corneal layer of blowfly’s eye from a single biotemplate. I was able to fabricate a nickel die that captured the 200-nm features found on the lenslets of a blowfly’s cornea, but I was not able to transfer these features to a replica by
casting. The future of this work is to use the nickel die in a stamping process that will allow the transfer of the fine features of the cornea. After high-fidelity replicas are produced they can be characterized and potential applications, such as a collector layer on photovoltaic devices, sought out.
Chapter 2

Modified-CEFR Technique

2.1 Premise for the modified-CEFR technique

In high-vacuum conditions, the thermally evaporated vapor flux is highly directional as a consequence of reduced scattering processes. As such, deposition rates and coating morphology are affected by the shape and the position of the biotemplate [14, 20, 21]. For a nonplanar biotemplate, one would expect the local average vapor flux direction (quantified by a locally varying angle $\chi_L$ analogous to $\chi_v$) to vary over the exposed surface of the biotemplate, thereby resulting in nonuniform deposition rates and coating morphology.

This premise led me to consider more closely the specific shape of a biotemplate, chosen as the compound eye of the blowfly *Phormia regina*. The compound eye of a blowfly is composed of many eyelets. The compound eye has an irregular shape best described as approximately a coronal frustum of an elongated ellipsoid. For simplicity, when describing the spatial variation of $\chi_L$, it may be best to consider only a transverse section of the compound eye. Figure 2.1 shows such a section. With $\chi_v$ fixed at $20^\circ$, $\chi_L$ can vary between $20^\circ$ and $110^\circ$. With such a range of directions of the incident vapor flux, the spatial variation in deposition rate and coating morphology could be very significant over the surface of the biotemplate.
In order to reduce the effect of the spatial variation in $\chi_L$, we can vary $\chi_v$ continuously in such a way that all regions of the biotemplate surface see $\chi_L$ as being continuously varied between $0^\circ$ and $90^\circ$. If the biotemplate shape is approximated as being hemispherical, by continuously oscillating $\chi_v$ between $10^\circ$ and $90^\circ$, the result will be that all regions of the sample will receive the same average vapor flux with the same average directionality, leading to a more uniform deposition rate and coating morphology.

2.2 Experimental procedure

2.2.1 Sample preparation

Blowflies were obtained by way of a simple trap. The trap consisted of a shallow Mason jar containing a mixture of beef liver, chicken liver, salmon, apples and brown sugar that was used as bait. When several flies would gather on the bait, a net would be placed over the open end of the jar. Once the open end of the jar was covered, the flies were startled by shaking the jar.
resulting in them flying into the net. The netted flies were then transferred to a second Mason jar containing a small amount of ethyl acetate on a cotton swab for the purpose of euthanization. The now dead blowflies were then placed in a jar containing ethyl alcohol to be stored for future use.

The blowflies were allowed to soak in ethyl alcohol for at least two weeks to ease dissection. The corneas were removed from the blowflies manually with the use of two pair of fine tweezers and a dissecting microscope. The dissection was done in ethyl alcohol to dampen motion and to clear unwanted material from the corneas. Dissection occurred in several steps beginning with removing the head from the thorax. The head was then separated laterally into halves and each half then further processed. Unwanted material was progressively stripped away until only the corneal layer of the blowfly eye remained. The corneal layers were then dried in air for 24 h. The final step in sample preparation was to attach the corneas to a microscope slide with double-sided tape. The slide was used as a planar substrate to be attached to the rotation platform during deposition. Figure 2.2 a-c shows photographs of a blowfly during various steps of preparation.

2.2.2 Thermal evaporation apparatus

The thermal evaporation system used for physical vapor deposition consisted of a vacuum chamber, a mechanical vacuum pump, a turbo-molecular vacuum pump, a high-current DC-power supply, two thermocouple pressure gages, an ion-pressure gage, a quartz-crystal thickness monitor, a source shutter, a platform to hold the planar substrate onto which the biotemplate was mounted, a stepper motor to control the angle $\chi_v$, a stepper motor to rotate the platform holding the substrate and the biotemplate, and a desktop computer to control both stepper motors.

2.2.3 Deposition of coating

In a high-vacuum environment, the corneas were coated using the original CEFR technique [4, 10, 11] and two modalities of the modified-CEFR technique, in order to compare the thickness unifor-
mity and coating morphology. Bulk chalcogenide glass with nominal composition Ge\textsubscript{28}Sb\textsubscript{12}Se\textsubscript{60} (Schott IG5) was thermally evaporated at base pressures between 1 and 4 \(\mu\)Torr and a deposition rate of 1 nm s\(^{-1}\). Chalcogenide glass was selected for its ease of thermal evaporation and mechanical properties [22]. Crushed chalcogenide glass was placed in a 12.5-mm wide tungsten boat that was heated by passing a current of between 75 A and 80 A. Several minutes were initially allowed for the voltage to stabilize; then the platform motion was initiated and the source shutter opened. Once the source shutter was open, the current was adjusted to bring the deposition rate to 1 nm s\(^{-1}\). Coating thickness and deposition rate were monitored \textit{in situ} by a quartz crystal monitor (QCM).

Computerized control of the two stepper motors located in the vacuum chamber allowed me to manipulate the platform during deposition. One of the two stepper motors allowed me to adjust the vapor flux angle \(\chi\). The second motor allowed for rotation about an axis normal to the platform. A combination of these two motions was used when implementing both the CEFR
and modified-CEFR techniques. In the CEFR technique, the platform was fixed at $\chi_v = 10^\circ$ and rotated about the normal axis at 2 rps. In the first modality of the modified-CEFR technique, $\chi_v$ was continually oscillated between $90^\circ$ and $10^\circ$ with a period of 9 s. In an attempt to further tune the motion of the platform to the shape of the biotemplate, a second modality was developed. In this modality, $\chi_v$ was repeatedly run through a three-step variation: it was first altered steadily from $90^\circ$ to $30^\circ$ in 1.67 s, then from $30^\circ$ to $10^\circ$ and back to $30^\circ$ in 2.22 s, and finally from $30^\circ$ to $90^\circ$ in 1.67 s.

### 2.3 Analysis of results

In order to evaluate the uniformity of thickness and morphology of the coatings deposited using the CEFR technique and the two modalities of the modified-CEFR technique, coated corneas were transversely sectioned and inspected with a scanning electron microscope (SEM).

#### 2.3.1 Microtomy

All coated corneas were encapsulated in a low-viscosity epoxy resin which was thermally cured for 24 h. Following encapsulation, each sample was transversely sectioned using a Leica UC6 Ultramicrotome. The resulting 1-$\mu$m-thick sections were then mounted on an aluminum target for imaging. During microtomy, the encapsulated and coated biotemplates were often fractured as can be seen in the SEM images presented next.

#### 2.3.2 Scanning electron microscopy

The transverse sections were imaged using a Hitachi S-3500N SEM. Four zones were designated on each transverse section for closer inspection. These zones were selected to collectively capture the shape of the biotemplate and its effects on coating thickness and morphology.

Figure 2.3 shows a collage of SEM images of a coating deposited by the CEFR technique.
Figure 2.4 and Figure 2.5 are similar to Figure 2.3 except these coatings were deposited by the first and second modalities, respectively, of the modified-CEFR technique described earlier in Section 2.2.

### 2.3.3 Results

In each zone numbered in Figures 2.3, 2.4, 2.5 and others, three measurements of thickness were made. To quantify the uniformity of coating thickness, we calculated the mean and standard deviation of coating thickness for each coated biotemplate. The results of these measurements are given in Figure 2.6 and Table 2.1 for two CEFR-produced coatings, two coatings fabricated using the first modality of the modified-CEFR technique, and one coating produced using the second modality of the modified-CEFR technique. These data demonstrate a roughly two-fold improvement in the uniformity of the coating thickness by using the second modality [19] over the original CEFR technique [4, 10]. Close inspection of Figure 2.3 reveals that the coating morphology varies between all four selected zones. The most notable variation occurs in zone 3 where $\chi_L$ is very acute. In fact, as the individual lenslet curves away as one looks at the left side of zone 3, that section of the eye is completely shadowed by the higher portions of the eye between it and the vapor source.

Figure 2.7 is a compilation of four different morphologies, three (a-c) of which were observed in CEFR-produced coatings and one (d) from a coating fabricated using the second modality of the modified-CEFR technique. Figure 2.7(a) shows a conical morphology that is often found in thermally evaporated films deposited at $\chi_L = 90^\circ$ [16, 23], Figure 2.7(b) is a magnified view from zone 3 of Figure 2.3 for a CEFR produced coating where $\chi_L = 0^\circ$, and Figure 2.7(c) shows the dense columnar morphology that is expected of a CEFR-produced film on a planar substrate. Finally, Figure 2.7(d) is an image of the typical morphology of a coating produced using the second modality of the modified-CEFR technique on a nonplanar substrate. Indeed, a careful examination of Figures 2.4 and 2.5 confirm that this type of dense morphology is produced in all
four zones.

Table 2.1. Average thickness and % standard deviation for coatings produced using (a), (b) the CEFR technique, (c), (d) the first modality modified-CEFR technique, and (e) the second modality modified-CEFR technique

<table>
<thead>
<tr>
<th>Deposition</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean (nm)</td>
<td>1323</td>
<td>1124</td>
<td>755</td>
<td>828</td>
<td>669</td>
</tr>
<tr>
<td>% St. Dev.</td>
<td>17</td>
<td>20</td>
<td>9</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>
Figure 2.3. Top row: Cross-sectional SEM image of a transverse section of a cornea first coated by the original CEFR technique and then encapsulated in a low-viscosity epoxy resin. Bottom two rows: High-magnification images of sections identified as 1–4 in the top image.
Figure 2.4. Same as Fig. 2.3, but with the first modality of the modified CEFR technique.
Figure 2.5. Same as Fig. 2.3, but with the second modality of the modified CEFR technique.
Figure 2.6. Average thickness and standard deviation for (a,b) two CEFR-produced coatings, (c,d) two coatings fabricated using the first modality of the modified-CEFR technique, and (e) one coating produced using the second modality of the modified-CEFR technique.
Figure 2.7. SEM images of (a–c) three coating morphologies produced using the CEFR technique, and (d) one produced using the second modality of the modified-CEFR technique.
Fabrication of an Insect Eye Die

3.1 Introduction

Recent efforts at bioreplication have been successful in reproducing many of the features and properties of the original biotemplate from which they were drawn, but in all cases known to me the replication techniques used have produced a single replica from a single biotemplate [6, 7, 8, 9]. This means that for every replica produced one biological specimen must be sacrificed. If the biotemplate is of a rare nature or if a large number of replicas are to be created, this immediately becomes prohibitive. If bioreplicated structures are ever to find applications, a method of bioreplication that is both sustainable and scalable must be developed. In essence a bioreplication technique that produces many high-fidelity replicas for the sacrifice of a single biotemplate is needed.

Immediately what comes to mind is a master replica produced from the biotemplate that can be used to produce many subsequent replicas. The progression of this line of thought leads to the possibility of implementation of techniques such as imprint lithography and nanocasting to biomimetics. The complicated aspects of both of these techniques is the production of the master die. In most cases the die is produced by removing material from a blank die by focused-
ion-beam (FIB) milling, conventional lithography, e-beam lithography, or direct laser writing. Of these techniques, only FIB milling is capable of producing three-dimensional nano-scaled structures such as those that would be found on a potential bioreplica. The time, cost, and complexity of rendering the biotemplate present problems that even a powerful technique like FIB milling would have difficulty overcoming.

In this chapter, I present a two step technique combining the modified-CEFR technique with nickel electroforming that was devised to produce a high-fidelity die of the cornea of a blowfly’s compound eye for eventually producing multiple replicas.

3.2 Background

Electroforming was discovered in 1837 and since then has become a widely used die-fabrication technique [24, 25]. Electroforming exhibits several exceptional capabilities, the most notable of which is the ability to produce high-precision structures that are useful for dies and molds. Also, electroforming produces structures that exhibit precise reproduction of surface details found on the mandrel. Finally, electroforming is capable of reproducing whatever complex shape that the mandrel takes [25]. In order to produce a high-fidelity die that can be used to produce multiple replicas of a biotemplate, all of these characteristics are critical. Biotemplates often have very fine structure and complicated shapes that are not easily produced synthetically. Along with these positive characteristics, electroforming also has drawbacks such as long deposition times, a small number of usable materials, and surface resolution limited by grain size [25].

The challenge to producing molds with micro-and nano-scaled features is producing the master or mandrel. These masters can be fabricated in several ways. One such method is hot embossing of a silicon master in a polymer which is then used as the mandrel for electroforming [26]. Another method of producing the mold is to make a negative by conventional, interference, or e-beam lithography and then using the silicon master as the mandrel for electroforming [27, 28]. Once
electroforming is completed, the silicon master can be etched away leaving behind the nickel die. My master will be produced by coating an array of compound eyes with a nickel layer by the modified conformal-evaporated-film-by-rotation technique. Traditionally, if the mandrel is non-conducting it is coated with a thin metal layer ($\approx 10\ \text{nm}$) and then electroformed. I deposited $\sim 250\text{-nm}$ of nickel on the master using the second modality of the modified-CEFR technique. The purpose of this thick nickel coating is that it ultimately becomes a portion of the die and, because it is amorphous, some of the problems of grain size on surface roughness of electroformed dies are alleviated.

### 3.3 Experimental procedure

#### 3.3.1 Sample preparation

Several corneas harvested from compound eyes removed from common blowflies ($\textit{Eucalliphora lilea}$) were mounted with double-sided tape on a borosilicate glass slide cut down to approximately $2.5\ \text{cm}^2$ area. The double-sided tape fastened the corneas to the glass slide and also served as a delamination layer that allowed the final die to be separated from the glass substrate more easily. Corneas were placed on the tape one at a time, back-filled with PDMS and arranged to form either a $2 \times 2$ or $3 \times 3$ rectangular array. Figure 3.1 shows a $3 \times 3$ array of mounted corneas, while Figure 3.2 shows a close-up photograph of an individual cornea from the array. The corneas were back filled with PDMS in order to eliminate the gaps around the base of the corneas when they were sitting on the substrate. This back-filling step was required to avoid holes that would occur in subsequent electroforming steps if voids were present. The back filling was done by placing the cornea on the double sided tape, inserting an insulin syringe through one of the gaps between the biotemplate and the tape, and injecting PDMS until the back side of the cornea was filled and a smooth edge formed around the base of the biotemplate. The PDMS was then cured at $60\ ^\circ\text{C}$ for 48 h. While the PDMS was curring it undesirably flowed to cover the upper surface of
the corneas that I intended to reproduce. This thin layer of PDMS was removed by cleaning the sample in an ultrasonic bath containing ethanol.

3.3.2 Modified-CEFR

After the array of corneas was mounted, a 200-300-nm thick nickel coating was thermally evaporated onto the array using a modified conformal-evaporated film-by-rotation technique. This technique allowed me to produce coatings that were uniform in both thickness and structure over the surface of the array. It should be noted that this nickel coating was a functional component of the die and did not just serve as a conducting layer for subsequent electroforming. Because the coating was deposited by thermal evaporation and at low temperatures, it was amorphous. The absence of grain structures allowed the features of the original sample to be captured without distortion. Figure 3.3 shows a $3 \times 3$ array of corneas with a nickel coating.
Figure 3.2. A higher magnification image of one PDMS-backfilled corneas shown in Figure 3.1.

Figure 3.3. An optical microscope image of a 3×3 array of PDMS-backfilled corneas after coating with nickel using the second modality of the modified-CEFR technique.
Figure 3.4. An optical microscope image of a 2×2 array of PDMS-backfilled eyes after they had been electroformed with a thick Ni layer.

3.3.3 Electroforming

Following the CEFR step the array of corneas was structurally reinforced by electroforming a 60-µm-thick nickel layer on top of the thermally evaporated nickel coating. Electroforming was done in a nickel sulfamate electrolytic solution that was mechanically agitated at room temperature. The electrical source for the plating was a DC power supply generating 2 mA of current monitored by a digital ammeter. The anode was a 20-cm²-area stainless steel plate, and the nickel-coated surface constituted by the glass substrate and the array of corneas acted as the cathode. The sample was plated under these conditions for roughly 7 days in order to achieve the desired thickness. Figure 3.4 and Figure 3.5, respectively, show the top side of a 2×2 and a 3×3 array of corneas after electroforming had been completed.
3.3.4 Removal of the biotemplate

After electroforming was completed the sample was removed from the plating solution, rinsed with deionized water, and washed in an ultrasonic bath containing deionized water for 20 min. The die was then separated from the glass substrate by running a razor between the tape delamination layer (double-sided tape) and the glass substrate. The tape could then be easily peeled off the die. The PDMS-backfill and the actual blowfly corneas were then removed with tweezers, leaving behind only the negative arrays of corneas preserved in a nickel die. Figures 3.6, 3.7, and 3.8 show the bottom side of a 3×3 die, a close-up-image of a cornea still in place, and a close-up-image of the die after the original biotemplate and the PDMS backfill have been removed.

3.3.5 Casting

The electroformed nickel die was filled with PDMS in order to evaluate how readily the features of the original cornea were captured in the die-making process. The PDMS was again cured at 60 °C for 48 h. After curing was complete, the PDMS was peeled away from the nickel die,
Figure 3.6. The underside of a $3 \times 3$ array of blowfly corneas after coating, electroforming and removal of some of the original corneas. In this photograph the corneas have been removed from the upper 2 rows to reveal the die, but left in place in the bottom row.

Figure 3.7. A higher-magnification photograph of the electroformed die with the biotemplate still in place.
yielding a $3 \times 3$ array of PDMS replicas.

### 3.4 Analysis and Results

Both the electroformed die and the PDMS replicas were imaged with an SEM in order to observe the presence of key features found on the original corneas.

#### 3.4.1 Die

The die was imaged with an SEM to evaluate the quality and fidelity of the details transferred between the original cornea and die. Figure 3.9 shows an 80× magnification image of the die. This image shows that the overall shape of the cornea is preserved during the modified-CEFR coating process and the subsequent electroforming step. Figure 3.10 shows a 500× magnification image where we can see the negative of the lenslets that compose the compound eye. In Figure 3.11 we see the approximately 200-nm features that pattern the surface of the individual lenslets also appear in the die.
Figure 3.9. An SEM image of one of the members of a $3 \times 3$ array shown at $80 \times$ magnification. Since this is a die, it appears as the negative of the biotemplate.

Figure 3.10. An SEM image of the die shown in Figure 3.9 at $500 \times$ magnification. In this image we can see that the negative of the 20nm lenslets are present in the die.
Figure 3.11. An SEM image of the die shown in Figure 3.10 at 20,000× magnification showing that the 200-nm features found on the lenslet are successfully captured in the modified-CEFR coating and transferred to the die.

3.4.2 Casting

After being peeled away from the electroformed die, several PDMS replicas were mounted for inspection by SEM. Figure 3.12 shows SEM images of a blowfly cornea and a PDMS casting at 65× magnification. These images confirm that the corneal surface has been reproduced on the mm scale and that evidence of the 20-µm lenslets is visible. A 1000× magnification SEM image of a blowfly cornea and a 650× magnification SEM image of the same PDMS replica are shown in Figure 3.13. Figure 3.14 shows a 2700× magnification SEM image of the PDMS replica. From these figures I conclude that the overall shape as well as the lenslets that comprise the blowfly cornea were successfully replicated in the PDMS castings. These figures also show that the 200-nm surface features of the original lenslets were not successfully transferred. Because the 200-nm features are present on the electroformed die a stamping process may be successful in transferring these features from the die to the polymer replica.
**Figure 3.12.** An SEM of a blowfly cornea (left) and a PDMS casting (right) at 65× magnification showing that the cornea is reproduced on the mm scale.

**Figure 3.13.** An SEM image of a blowfly cornea at 1000× magnification (left) and an SEM image of a PDMS casting at 650× magnification (right) showing that 20-µm diameter lenslets are roughly reproduced in the PDMS casting.
Figure 3.14. An SEM image of the PDMS casting at 2700× magnification showing that the boundaries between lenslets are not well defined.
Chapter 4

Misfires

Each step in the process of fabricating the die of an array of blowfly corneas presented some challenges. Most of these challenges arose from the considerations that had to be made for the process to be compatible with the biolotemplate. Here I discuss several techniques I tried that turned out to be dead ends.

4.1 Evaporation

There were many challenges to thermally evaporating nickel due to its high temperature at vapor pressure and its tendency to wet the surface of the thermal source. My initial attempt to evaporate nickel was by using single-conductor tungsten baskets with nickel pellets. Attempting to evaporate the nickel in this way led to the baskets burning out, once the nickel had melted and wetted the surface. The basket would burn out at the edge of the nickel melt. I then attempted to use a three-conductor tungsten basket but the result was the same. At this point I abandoned the baskets for a narrow tungsten boat to evaporate the pellets. This also did not work; the most common failure was the boat burning out where it came in contact with a pellet. Hence, I decided to try an alternative to the pellets as the source material. I now attempted to use
nickel wire arranged in several ways in the tungsten baskets. The wire was coiled into a loose ball, a tight cylinder, and even around the tungsten basket, but all of these attempts lead to the baskets burning out. As a final attempt at using the tungsten baskets, the wire was cut into approximately 1-cm lengths and placed loosely in the basket. Again, the baskets would burn out as soon as the nickel would melt and wet the surface.

I then went to the combination of nickel wire and narrow tungsten boats. The same wire wrappings that were attempted for the baskets were repeated for the boat. Some success was had with the wire wrapped into a tight cylinder and placed on the tungsten boat, if the boat was rapidly heated to allow the wire to melt before causing hot zones to form in the boat. As this method was successful sporadically, I continued the search for an alternative method.

The configuration that was ultimately found to be successful was to take four pieces of nickel wire that were approximately 4 cm in length, twist them together, and place them lengthwise on the narrow tungsten boat. My best guess as to why this worked better than the other configurations is that twisting the wires together made them melt at the same time. Also, by distributing the nickel over the boat no single high current regions were formed, thereby reducing the chances of burn troughs in the boat.

4.2 Mounting

Because of the irregular shape of the blowfly corneas, there were voids around the base of the cornea placed on a flat substrate. These voids would lead to holes being formed in the die during electroforming. In order to avoid the formation of these holes, I decided to prevent the voids by filling the back side of the cornea with a material that would fill the gaps around the base of the cornea and also be easily removed after the die was formed.

The first class of materials I tried were a series of two-part epoxies. The epoxies filled the voids nicely but were not easily removed from the die after electroforming. In the search for an
alternative to the epoxies, I tried PDMS. The PDMS was promising because, like the epoxies, it effectively filled the voids and is known to be a material that could be easily mechanically removed. The problem I ran into with PDMS was that it would undesirably diffuse over the upper sides of the corneas. The problem was compounded by the fact that the layer that was formed on the upper side of the corneas would not fully cure but leave behind a viscous residue. Attempts were made to remove this residue both mechanically and with common solvents with no success, and PDMS was shelved for the time being.

I went on to attach the eyes with several types of paints and glues but they all had their own problem such as melting during deposition or dissolution when placed in the electroforming bath. With the search for a better mounting material failing I returned to PDMS. After several days of experimenting with various solvents in an ultrasonic bath, it was found that 20-min ultrasonic cleaning in ethanol would remove the uncured residue without doing any noticeable damage to either the corneas or the cured PDMS. I now had a reliable way of mounting the corneas which eliminated the voids and could easily be removed after electroforming.

4.3 Removing the cast replicas

One of the lingering challenges of producing the PDMS replicas by casting is how to remove a replica from the die. PDMS was selected as the casting material because it is usually easy to pull it away from a die. In my first attempt at removing the cast from the die I found that the PDMS would rip, leaving large portions of the replica behind in the die. In an effort to help the PDMS release from the die, I dip-coated the die in a concentrated surfactant. The result was disappointing and the castings did not release any more readily than without the dip-coating.

With the problem of the PDMS ripping persisting, I attempted to cause the cast to release by swelling the PDMS. Chloroform, ethyl acetate, and acetone were all used to make the cast to swell out of the die. While the PDMS did swell in the die, it did not cause the PDMS to release.
Moving in the opposite direction, I attempted to cause the PDMS to release by cooling it to liquid-nitrogen temperature with the hope that it would contract enough to release from the surface of the die. This was again unsuccessful in causing the cast to release. Ultimately, I proceeded with manually pulling the castings from the die.

A potential solution to this problem may be to coat the die with a release layer such as Teflon. Other materials such as PMMA may also be used to cast the replicas and may more readily release from the die.
Concluding Remarks

5.1 Motivation

In its infancy, bioreplication shows promise as a concept and as a developing field that will lead to the invention of novel devices and solutions to existing engineering challenges. To date, bioreplication techniques have been able to produce a single replica from a single biotemplate. For bioreplication to become a feasible method of reproducing structures of interest found in nature, methods of mass producing replicas are necessary. This essentially excludes all methods that are only able to produce a single replica for the loss of a single biotemplate. My motivation for this research was to develop a method of producing many high-fidelity replicas for the sacrifice of a single biotemplate.

5.2 Accomplishments

I was able to modify the conformal-evaporated-film-by-rotation technique to improve coating thickness and morphology uniformity on nonplanar biotemplates such as the cornea of a blowfly’s eye. By making simple considerations of biotemplate geometry, I was able to reduce the variation
in film thickness by a factor of 2 while also creating a dense columnar morphology over the entire surface of the cornea. These improvements will result in a more robust and accurate replica of the biotemplate without contributing additional complexity or cost to the process. The standout feature of the CEFR replication technique is that it can be done in a matter of hours while still capturing the fine features of the biotemplate. In addition to being a rapid process it is also very cost efficient and flexible. With the CEFR technique I am able to transition from making chalcogenide glass replicas to metallic replicas or any other material that can be thermally evaporated by simply replacing the source material. Improvements in the CEFR technique and resulting coatings will lead to improvements in subsequent devices that may be fabricated from the replicas. Such devices may be light-harvesting devices, wide-acceptance-angle lenses, optical reflectors, antireflective coatings, or serve, as demonstrated here, as the master in a die-making process.

By using the modified-CEFR technique to produce a high-fidelity initial coating of a metal and then structurally reinforcing it through electroforming, I was able to fabricate robust metallic dies of arrays of blowfly corneas. The die was shown to capture features of the corneas on several scales simultaneously. The dies produced were 2×2 and 3×3 arrays of corneas demonstrating that dies from assemblies of many biotemplates can be fabricated.

I used the die to produce polymer replicas of the arrays of corneas by casting. The resulting replicas captured the mm and µm scale features of the corneas but the 200-nm scale features were not found in the replicas. It is possible that using a stamping method rather than casting would impress the fine features into the polymer replicas.

The robust nature of the nickel die means that it can be used to produce multiple replicas. This is essential to any bioreplication technique because any application will require a large number of replicas that can not be produced by replicating biotemplates one at a time.
5.3 Extensions

The future of this work is in the refinement of the casting method to achieve transfer of the 200-nm-scale features from the die to the replica. Following this, the optical properties of the replicas can be characterized and compared to those of a blowfly’s cornea. Specifically, the replica’s transmission spectra and light-trapping performance are of interest. If a study of the replica’s light-trapping performance shows merit for use of the replicas, applications such as light-harvesting layers in photovoltaic devices may be developed. Such layers may be directly patterned in crystalline silicon cells or impressed in the window layer of thin-film cells.

Another potential extension of this work could be a layer-by-layer stamping process to build up three-dimensional bioreplicated structures. An example of such a process would be to alternate between imprinting the stamp in a layer, and filling the negative space with an etchable material until the desired structure is produced. The etchable material that is filling the negative space could then be removed, leaving behind the desired three-dimensional structure. Specifically, this type of fabrication scheme could be useful in the production of visible-frequency photonic crystals.
Extra Figures

Figure A.1. An SEM image showing the fine features that pattern the surface of the lenslet of a blowfly cornea (shown at 40,000× magnification)
Figure A.2. A photograph taken with an optical microscope of a chalcogenide replica of the cornea of a blowfly’s eye. Note the interference fringes on the lenslets.

Figure A.3. A photograph taken with an optical microscope of a microtome section of a coated cornea.
Figure A.4. A collage of SEM images taken of a microtome section of a cornea that had collapsed prior to coating. The modified-CEFR technique produced uniform thickness and morphology even on this odd shape.

Figure A.5. An SEM image showing a die that was produced from a cornea that had the uncured PDMS on its surface.
Figure A.6. The same as Figure A.5 but at higher magnification.
Improved conformal coatings by oblique-angle deposition for bioreplication
Improved conformal coatings by oblique-angle deposition for bioreplication

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The conformal-evaporated-film-by-rotation (CEFR) technique, a bioreplication method to produce high-fidelity conformal coatings on biotemplates by oblique-angle deposition, was modified to improve the uniformity of coating thickness. The substrate holding the biotemplate was rocked, in addition to rotating it about an axis passing normally through it. With the compound eyes of the common blow fly as the biotemplate, quantitative comparison of coating thickness obtained by the original CEFR and the modified CEFR techniques showed the superiority of the latter.


Scientists and engineers are increasingly looking toward nature for both inspiration and templates that can be utilized for development of multifunctional, efficient, and miniature devices.1 Clearance of the first hurdle in bioreplication requires the development of techniques for creating the replicas of biological structures. Although bioreplication is still in an embryonic stage, uses of ion milling, lithography, casting, and vapor deposition have been reported thus far.2–6 As these fabrication tools advance, new fronts for biologists, physicists, and engineers to discover and design will open.

A desirable bioreplication technique must be simple, well-understood, reliable, and inexpensive. Oblique-angle deposition (OAD) helps fulfill these criteria.7,8 A variant called the conformal-evaporated-film-by-rotation (CEFR) technique was recently formulated to rapidly replicate biotemplates with high fidelity. In this technique, the biotemplate is mounted on a planar substrate that is rapidly rotated about an axis passing normally through it, while a thermally generated vapor flux of a chosen material is directed obliquely, at a fixed angle \( \chi_v \) \((0^\circ, 90^\circ)\) with respect to the substrate plane, toward the biotemplate, as shown schematically in Fig. 1(a). A replica is obtained when the \( \approx 500\)-nm-thick coating formed on the biotemplate is separated from the biotemplate. Till date, this technique has been applied for replicating the compound eyes of tephritid flies5 and the wings of butterflies,6,9 without compromising their optical characteristics that are due to nanoscale (<100 nm) structural features. This is because OAD produces nanoscale columnar thin films on the biotemplate.

The attractive features of the CEFR technique are as follows: (i) deposition occurs near the ambient temperature, (ii) the deposition rate can be several \( \text{nm s}^{-1} \), and (iii) no chemicals are present so that the biotemplate is not altered during deposition. Accordingly, this technique has a great potential to make inorganic replicas that exhibit greater chemical and mechanical robustness than the original biotemplates. The enhanced robustness would allow a replica to be used as a free-standing optical device or as a master die in an imprint lithography technique for mass replication.10

The prospect of additional functionalities being engendered by the material used for replication may lead to replicas with enhanced characteristics over the original template.

As thermally generated vapor flux in high vacuum is directional, the deposition rate, and coating morphology on the planar substrate are greatly affected by the angle \( \chi_v \).8,12 In general, small-\( \chi_v \) deposition yields thin porous coatings, while high-\( \chi_v \) deposition creates thick dense coatings, when the substrate is stationary. This observation conforms to the relationship \( \rho \propto (1+\sin \chi_v)^{-1}\sin \chi_v \), determined in the absence of substrate rotation and rocking for the mass density \( \rho \).13 Moreover, the measured atomic density and the constitutive parameters of GeSbSe columnar thin films agree well with this relationship and the composition is independent of \( \chi_v \).14

The dependence of porosity upon \( \chi_v \) becomes complicated when a nonplanar biotemplate is mounted on the substrate, FIG. 1. (Color online) (a) Schematic of the CEFR technique. (b) Variation of \( \chi_v \) at four locations on a lateral section of the compound eye, while the angle \( \chi_o \) is fixed in the original CEFR technique.

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and even more so when the biotemplate surface is structured at the nanoscale. Even though $\chi_v$ is fixed in the CEFR technique, the angle $\chi_L$ between the vapor-flux direction and the tangent plane at a location on the biotemplate surface can vary significantly from location to location, as shown in Fig. 1(b) for a coating produced on the eye of a common blow fly. Thus the deposition rate as well as the porosity vary over the biotemplate.

In order to reduce the effect of the variation in $\chi_L$ over the biotemplate, we decided that $\chi_v$ must be varied in time such that $\chi_L$ at any location on the biotemplate also varies temporally during deposition. The temporal variation of $\chi_L$ could significantly offset its spatial variation so that the vapor fluxes received at all locations on the biotemplate have the same time-averaged direction, and the coating is formed everywhere with the same average deposition rate. This model neglects the variable shadowing$^{8,12}$ that occurs as the substrate is rotated about the substrate normal. Also, several different temporal variations of $\chi_v$ may have to be tried to gain control over the degree of uniformity of coating thickness.

The CEFR technique was modified by introducing a second degree of freedom to the substrate motion during deposition. The first degree, as in the original CEFR technique, is the rotation of the substrate about an axis passing normally through it. The second degree is the rocking of the substrate about an axis lying wholly in the substrate plane so as to continuously vary $\chi_v$ during deposition. The biotemplate selected was the compound eye of a common blow fly. The compound eye presents a challenge because (i) it possesses both micro and nanoscale features that would have to be preserved by the conformal coating, and (ii) it is a curved surface on the macroscopic scale.

Bulk chalcogenide glass with composition $\text{Ge}_{25}\text{Sb}_{12}\text{Se}_{60}$ was used as the source material for all depositions. This glass was selected for ease of deposition and its mechanical robustness.$^{15}$ All film depositions were by resistive thermal evaporation at base pressures between 1 and 4 $\mu$Torr, and a nominal deposition rate of $\sim$1 nm/s. Typical coating thickness, as reported by a quartz crystal monitor, was set at $\sim$800 nm, a relatively thick coating being needed for enough mechanical strength to allow subsequent handling to obtain a replica.

For the analysis of the coatings, samples were first encapsulated in a low-viscosity epoxy resin and then laterally sectioned into 1-µm-thick slices using a Leica UC6 Ultramicrotome. Several sections were mounted on aluminum holders for imaging to be carried out. Scanning-electron microscope (SEM) characterization was performed using a Hitachi S-3500N SEM.

We coated the compound eyes by both the CEFR technique$^{5,6,9}$ and the modified CEFR technique to allow comparison of film thickness and overall uniformity. For both techniques, the substrate was rotated about the normal axis at 2 rps. When implementing the CEFR technique, we fixed $\chi_v = 10^\circ$. Two modalities of the modified CEFR technique were implemented. In the first modality, $\chi_v$ was continually oscillated between 90° and 10° with a temporal period of $\sim$9 s. With the experience gained therefrom, we designed the second modality as a three-step oscillation; $\chi_v$ was varied continuously from 90° to 30° in 1.67 s; then from 30° to 10° and back to 30° in 2.22 s; and finally from 30° to 90° in 1.67 s.

Coating uniformity was evaluated by obtaining SEM images of the lateral sections of coated eyes. The SEM images allowed us to inspect the coating morphology and also directly measure the thickness. Four zones were selected from which thickness measurements were taken for all selected sections. The zones were selected to highlight how biotemplate shape affects coating deposition. Figure 2 is a collage of cross-sectional SEM images of a representative section of coatings deposited by the CEFR technique, and Fig. 3 presents a similar collection of images but for the modified CEFR technique of the second modality. The SEM images are arranged and numbered to facilitate direct comparison of similar regions on the compound eye. Parenthetically, we note the clearly evident columnar morphology of the coating in Fig. 2.

A comparison of Figs. 2 and 3 clearly shows that the coatings deposited by the modified CEFR technique are denser and of more uniform morphology than those produced using the original CEFR technique. In this respect, it is worth noting that cracking of the coatings into chunks is
due to the unavoidable damage caused by the microtome sectioning process. As a quantitative comparison of the two techniques, the average thickness and percent standard deviation are presented in Table I for [(a) and (b)] two sections coated using the original CEFR technique, [(c) and (d)] two sections coated using the first modality of the modified CEFR technique, and (e) a section coated using the second modality of the modified CEFR technique.

<table>
<thead>
<tr>
<th>Deposition</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean (nm)</td>
<td>1323</td>
<td>1124</td>
<td>755</td>
<td>828</td>
<td>669</td>
</tr>
<tr>
<td>% Standard deviation</td>
<td>17</td>
<td>20</td>
<td>9</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>

In summary, we used a simple geometric conception to identify steps that can be taken to improve the quality of coatings deposited on biotemplates by the CEFR technique. By modifying the CEFR technique and analyzing SEM images of the resulting coatings, we confirmed that substrate motion can be tailored to the shape of a biotemplate in order to achieve a more uniform coating. Although we chose the compound eye of the common blow fly as a biotemplate for this work, our results should hold for biotemplates in general. Replicas derived from more uniform coatings would be more robust to handle as dies during imprint lithography for mass bioreplication.

Appendix C

Modification of

conformal-evaporated-film-by-rotation

 technique to improve uniformity of

replicas of nonplanar biotemplates
Modification of conformal-evaporated-film-by-rotation technique to improve uniformity of replicas of nonplanar biotemplates

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ABSTRACT

We modified the conformal-evaporated-film-by-rotation (CEFR) technique to improve the uniformity of nominally $<1000$-nm-thick films deposited on nonplanar biological templates to replicate surface features. The biotemplates selected are eyes harvested from \textit{Phormia regina}, a common species of blow fly which has large compound eyes. Bulk chalcogenide glass with nominal composition Ge$_{28}$Sb$_{12}$Se$_{60}$ was used as the source material for all coatings. The modified CEFR technique introduced a second degree of freedom in manipulating the biotemplate with respect to the average direction of the vapor flux. We were thus able to tailor the motion of the platform holding the biotemplate to improve the uniformity of the coatings. Cross-sectional images of the coated biotemplates obtained using microtomy and scanning electron microscopy confirmed the expected improvement.

Keywords: Biomimetics, bioreplication, conformal thin film, physical vapor deposition, replica

1. INTRODUCTION

Nature has produced a vast array of structures, the variety of which science will probably never match; every organism is a marvel of specialized features that engendered its emergence and will probably prolong its survival. Engineers and scientists are increasingly drawing inspiration from nature for novel devices or structures to improve existing technologies and create new technologies.\textsuperscript{1–6} This idea of mimicking nature is not new. One could argue that the first arrowhead was crafted to mimic the functionality if not the form of a predator’s claw, or that people spent centuries working to achieve flight inspired all along by the ability of birds to simply pass over obstacles impassable to land-locked humans.

The new feature of biomimetics is the ability to design and produce micro- and nano-scaled features and devices. Feynman famously said in 1959 that there is plenty of room at the bottom,\textsuperscript{7} which statement applies as much to biomimetics now as it did to nanotechnology\textsuperscript{8} then. The variety of microstructures in nature is staggering! Inspection via electron microscopy shows that nearly every insect has one or more remarkable microstructures, the most apparent of which are diffraction gratings that cause many insects to exhibit some degree of iridescent coloration.\textsuperscript{4, 9}

Identifying the natural structures that may be of some use initiates biomimetics. For the most part, biomimetics research has centered on \textit{bioinspiration}: first drawing inspiration from a natural structure for its specific functionality, and then designing and fabricating a structure that exhibits a similar functionality.\textsuperscript{10} In contrast, the approach which some researchers are taking these days is \textit{bioreplication}: direct replication of structures found in natural organisms.\textsuperscript{5, 6} That is to say they are attempting to directly copy these natural structures with the highest fidelity they can achieve.

The toolbox for copying these structures is currently very similar to that for fabricating semiconductor devices. Lithography, physical vapor deposition, chemical vapor deposition, atomic layer deposition, focused

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ion-beam technique, and variants of the basic sol-gel method have all been used in biomimetics by various researchers.\textsuperscript{11–14}

The technique we employ to achieve direct, high-fidelity replication of biological surfaces is a physical-vapor-deposition method dubbed the conformal-evaporated-film-by-rotation (CEFR) technique.\textsuperscript{14–17} This technique is an offshoot of the oblique-angle deposition (OAD) technique. Usually in OAD, a planar substrate is held on a platform at an angle $\chi_v$ with respect to the average direction of a directional vapor flux, as shown in Fig. 1(a), in a vacuum chamber. Under the right conditions, the film deposited on the substrate is an array of parallel columns that are tens of nanometers in diameter and inclined with respect to the substrate by an angle equal or larger than $\chi_v$.\textsuperscript{18, 19} Such a thin film is called a columnar thin film (CTF).\textsuperscript{20, 21} If the platform holding the planar substrate is slowly rotated about a normal axis, the columns formed are like corkscrews, and the deposited film is called a chiral sculptured thin film.\textsuperscript{20} If the platform is rotated rapidly during deposition, the corkscrews coalesce into columns tilted normally to the planar substrate.\textsuperscript{22}

![Figure 1](image-url)

**Figure 1.** Schematics of (a) the OAD and (b) the CEFR techniques.

The CEFR technique involves rapid rotation rotation of the platform to which is affixed a nonplanar substrate, such as a biotemplate, as shown in Fig. 1(b). For bioreplication, a film of thickness $\lesssim 1000$ nm is usually deposited—the thinner, the better.

The array of parallel upright nanoscale columns is analogous to a pin toy.\textsuperscript{20} When the pin toy is placed on top of an object the topography of the object is transferred along the pins to the upper surface. The resolution of the reproduction created by the upper side of the pins is determined by the diameter of the pins. The upright columns produced by the CEFR technique constitute a pin-toy replica with pin diameter of tens of nanometers.\textsuperscript{23} The small columnar diameter and rapid rotation of the platform allow us to conformally coat many types of nonplanar substrates. To date, the CEFR technique has been successful in reproducing the structures found on: the wings of butterflies\textsuperscript{15, 16} and moths,\textsuperscript{14} the compound eyes of fruit flies,\textsuperscript{14} and blow flies,\textsuperscript{24} electronic comb resonators.\textsuperscript{17}

The advantages that the CEFR technique holds over other bioreplication methods are as follows: the sample (biotemplate) remains near ambient temperature during deposition, the deposition rate can be tens of angstroms per second, and the process is entirely physical.\textsuperscript{18, 19} Low temperature is critical when working with biological samples that can be damaged by high temperatures. A reasonable deposition rate is key in any process that is to be implemented on an industrial scale. As with temperature, the absence of caustic precursors helps to ensure that the sample is not altered during the deposition process.

After separation from the biotemplate, a coating becomes a replica.\textsuperscript{14, 16} A replica may be used as freestanding optical device. Many potential applications for CEFR-produced replicas require them to be very uniform in thickness and structurally robust. As such, it became pertinent to take a closer look at the uniformity of both thickness and morphology of CEFR-produced coatings. We found these coatings to have poor uniformity in both thickness and film structure, when the biotemplate is significantly nonplanar, which prompted us to modify the CEFR technique to rectify these shortcomings. The resulting modified-CEFR technique resolves these issues with the original CEFR technique. Here we show how a consideration of the shape of the biotemplate and tailoring the motion of the platform holding the biotemplate can result in coatings with improved uniformity in thickness and morphology.

## 2. PREMISE FOR MODIFIED-CEFR TECHNIQUE

In high-vacuum conditions, the thermally evaporated vapor flux is highly directional as a consequence of reduced scattering processes. As such, deposition rates and film morphology are mainly affected by the shape and the...
position of the biotemplate.\textsuperscript{19, 25, 26} For a nonplanar biotemplate, one would expect the local average vapor flux direction (quantified by a locally varying angle $\chi_L$ analogous to $\chi_v$) to vary over the exposed surface of the biotemplate, thereby resulting in nonuniform deposition rates and film morphology.

This premise led us to consider more closely the specific shape of a biotemplate, chosen as the compound eye of the blow fly \textit{Phormia regina}. The compound eye of a blow fly is made of many eyelets. The compound eye has an irregular shape best described as approximately a coronal frustum of an elongated ellipsoid. For simplicity, when describing the spatial variation of $\chi_L$, it may be best to consider only a transverse section of the eye. Figure 2 shows such a section. With $\chi_v$ fixed equal to 20$^\circ$, $\chi_L$ can vary between 20$^\circ$ and 110$^\circ$. With such a range of directions of the incident vapor flux, the spatial variations in deposition rate and film morphology could be very significant over the surface of the biotemplate.

In order to reduce the effect of the spatial variation in $\chi_L$, we can vary $\chi_v$ continuously in such a way that all regions of the biotemplate surface see $\chi_L$ as being continuously varied between 0$^\circ$ and 90$^\circ$. If we approximate the biotemplate shape as hemispherical, by continuously oscillating $\chi_v$ between 10$^\circ$ and 90$^\circ$ the result will be that all regions of the sample will receive the same average vapor flux with the same average directionality, leading to a more uniform deposition rate and film morphology.

3. EXPERIMENTAL PROCEDURE

3.1. Sample Preparation

Figures 3(a-c) show three stages during sample preparation, which began by collecting specimen of \textit{P. regina} on and in the vicinity of the University Park campus of Penn State. Blow flies were baited with a cocktail of beef liver, chicken liver, salmon, apples, and brown sugar left in the sun to putrefy. The trap consisted of a shallow mason jar containing the bait. When half a dozen flies would congregate on the bait a net would be placed over the open end of the jar. The flies would be then startled by shaking the jar, thereby causing them to fly up into the net. The netted flies would then be transferred to a second jar containing a cotton swab with a small amount of ethyl acetate. Once the flies lost consciousness, they were placed in a third jar containing ethyl alcohol in which they were preserved for future use.

Soaking the flies in ethyl alcohol for two weeks eased the task of dissection. The eyes were manually harvested using two pairs of fine tweezers under a dissecting microscope. The harvested eyes remained immersed in ethyl alcohol during dissection to dampen motion and also to prevent them from sticking to the tweezers. The dissection process began by removing the head from the thorax. The head was then separated laterally into halves, and each half separately processed further. Unwanted material was progressively stripped away until only the corneal layer of the eye remained. The eye was then allowed to dry in air for 24 h. The final step in sample preparation was to attach the eye to a microscope slide with double-sided tape. The slide acts as a planar substrate to be attached to the platform during deposition.

3.2. Thermal-Evaporation Apparatus

The thermal evaporation system consists of a vacuum chamber, a mechanical vacuum pump, a turbo-molecular vacuum pump, a high-current DC-power supply, a thermocouple and two ion-pressure gauges, a quartz-crystal thickness monitor, a source shutter, a platform to hold the planar substrate on which the biotemplate is mounted, a stepper motor to control the angle $\chi_v$, a stepper motor to rotate the platform holding the biotemplate, and a desktop computer to control both stepper motors.
3.3. Deposition of Coating

In a vacuum chamber, fly eyes were coated using the original CEFR technique and two modalities of our modified-CEFR technique, in order to compare the thickness uniformity and film morphology. Bulk chalcogenide glass with nominal composition $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ was thermally evaporated at base pressures between 1 and 4 $\mu\text{Torr}$ and a deposition rate of 1 nm s$^{-1}$. Chalcogenide glass was selected for its ease of thermal evaporation and mechanical properties. Crushed chalcogenide glass was placed in a 12.5-mm wide tungsten boat that was heated by passing a current of between 75 A and 80 A. First several minutes were allowed for the voltage to stabilize; then the platform motion was initiated and the source shutter opened. Once the source shutter was open, the current was adjusted to bring the deposition rate to 1 nm s$^{-1}$. Film thickness and deposition rate were monitored in situ by a quartz crystal monitor.

Computerized control of the two stepper motors located in the vacuum chamber allows us to manipulate the platform during deposition. One of the two motors lets us adjust the vapor flux angle $\chi_v$. The second motor allows for rotation about an axis normal to the platform. A combination of these two motions was used when implementing both the CEFR and the modified-CEFR techniques. In the CEFR technique, the platform was fixed at $\chi_v = 10^\circ$ and rotated about the normal axis at 2 rps. In the first modality of the modified-CEFR technique, $\chi_v$ was continually oscillated between 90$^\circ$ and 10$^\circ$ with a period of 9 s. In an attempt to further tune the motion of the platform to the shape of the biotemplate, a second modality was developed. In this modality, $\chi_v$ was repeatedly run through a three-step variation: it was first altered steadily from 90$^\circ$ to 30$^\circ$ in 1.67 s, then from 30$^\circ$ to 10$^\circ$ and back to 30$^\circ$ in 2.22 s, and finally from 30$^\circ$ to 90$^\circ$ in 1.67 s.

4. ANALYSIS OF RESULTS

In order to evaluate the uniformity of thickness and morphology of the coatings deposited using the CEFR technique and the two modalities of the modified-CEFR technique, coated eyes were transversely sectioned and inspected with a scanning electron microscope (SEM).

4.1. Microtomy

Figure 3(d) shows a coated eye. All coated biotemplates were encapsulated in a low-viscosity epoxy resin which was thermally cured for 24 h. Following encapsulation, each sample was transversely sectioned using a Leica UC6 Ultramicrotome. The resulting 1-µm-thick sections were then mounted on an aluminum target for imaging. During microtomy, the encapsulated and coated biotemplates were often fractured, as can be seen in the SEM images presented next.
**Figure 4.** Top row: Cross-sectional SEM image of a transverse section of a compound eye first coated by the original CEFR technique and then encapsulated in a low-viscosity epoxy resin. Bottom two rows: High-magnification images of sections identified as 1–4 in the top image.

**Figure 5.** Same as Fig. 4, but with the second modality of the modified CEFR technique.
4.2. Scanning Electron Microscopy

The transverse sections were imaged using a Hitachi S-3500N SEM. Four zones were designated on each transverse section for closer inspection. These zones were selected to collectively capture the shape of the biotemplate and its effects on film thickness and morphology. Figure 4 shows a collage of SEM images of a coating deposited by the CEFR technique. The SEM images are numbered such that the zones indicated in the figure in the top row correspond to the numbered high-magnification images in the bottom two rows of the collage. Figure 5 is similar to Fig. 4, except this film was deposited by the second modality of the modified-CEFR technique described earlier.

4.3. Results

In each zone numbered in Figs. 4, 5 and others, three measurements of thickness were made. To quantify the uniformity of film thickness, we calculated the mean and standard deviation of film thickness for each coated biotemplate. The results of these measurements are given in Fig. 6 for two CEFR-produced coatings, two coatings fabricated using the first modality of the modified-CEFR technique, and one coating produced using the second modality of the modified-CEFR technique. These data demonstrate a roughly twofold improvement in the uniformity of the coating thickness by using the second modality over the original CEFR technique.

Close inspection of Fig. 4 reveals that the film morphology varies between all four selected zones. The most notable variation occurs in zone 3 where \( \chi_L \) becomes very acute. In fact, as the individual eyelet curves away as one looks at the left side of zone 3, that section of the eye is completely shadowed by the higher portions of the eye between it and the vapor source. Figure 7 is a compilation of four different morphologies, three (a–c) of which were observed in CEFR-produced coatings and one (d) from a coating fabricated using the second modality of modified-CEFR technique. Figure 7(a) shows a conical morphology that is often found in thermally evaporated films deposited at \( \chi_L = 90^\circ \).21, 29 Fig. 7(b) is a magnified view from zone 3 of Fig. 4 for a CEFR-produced coating where \( \chi_L = 0^\circ \), and Fig. 7(c) shows the dense columnar morphology that is expected of a CEFR-produced film on a planar substrate. Finally, Fig. 7(d) is an image of the typical morphology of a coating produced using the second modality of the modified-CEFR technique film on a nonplanar substrate. Indeed, a careful examination of the images in Fig. 5 confirms that this type of dense morphology is produced in all four zones.

5. CONCLUDING REMARKS

The improvements in coating uniformity that result from modifying the CEFR technique will allow for the development of subsequent devices that exploit these coatings. Such devices may light-harvesting devices based on the functionality of blow-fly eyes or optical reflectors whose wide-angle functionality stems from natural photonic crystals.5, 30 In all of these cases the dense, uniform, columnar coating produced by the modified-CEFR technique will result in a more robust and accurate replica of the biotemplate. The standout feature of the CEFR-produced coatings (and replicas therefrom) is the rapidity of production, greatly facilitated by the wealth of knowledge collectively acquired about the OAD technique in general over a century and a half, at which they can be produced. A CEFR-produced coating can be fabricated in a matter of hours while still capturing the micro- and nano-scaled features that are present on the surface of the biotemplate. In the area of bioreplication, the CEFR technique is a very promising replication technique because of its low cost, simplicity, and quality of replicas produced.
Figure 7. SEM images of (a–c) three coating morphologies produced using the CEFR technique, and (d) one produced using the second modality of the modified-CEFR technique.

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Bioreplication is an emerging field where scientists and engineers are working to directly reproduce structures found in nature for the purpose of using them to both improve existing and develop novel devices. By directly replicating the biological structures I hope to maintain their naturally optimized form and functionality. Specifically, I have developed a method of producing many replicas from a single biotemplate. This is advantageous because existing bioreplication methods require a single biotemplate to be sacrificed for the production of a single replica. As this is not obviously scalable to manufacturing, the development of a method that is potentially scalable to these levels is a key step along the road to bioreplica-based devices.

I modified a thin-film deposition technique to improve its suitability for coating surfaces of biological samples. With these improved coatings I was able to create a high-fidelity metallic die that captures the features of a blowfly's cornea on the mm-µm- and the ~ 100nm scales simultaneously. From the die I was able to cast many polymer replicas that exhibited the mm and µm features of the original biotemplate. With further work it may be possible to capture the higher-resolution features in the polymer by using a stamping process rather than simple casting. Such replication processes may lead to inexpensive fabrication of micro-lens arrays, wide-acceptance-angle lenses for small covert cameras, or bioreplicated collector layers on the
exposed surfaces of solar cells.
Bibliography


