Interactions Between Suspended Nanowires and Patterned Surfaces**

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Gold nanowires, 350 nm in diameter and 3–6 μm in length, were derivatized by using positively and negatively charged self-assembled monolayers. The interactions between these particles and surfaces were investigated as a function of their surface chemistry and topography. Electrostatically repulsive sulfonate–sulfonate interactions resulted in mobile particles on the surface, whereas electrostatically attractive interactions between polyanamines and sulfonates immobilized the particles. Patterned surfaces were selectively derivatized with particles using these attractive and repulsive interactions. By lithographically defining surface wells that were commensurate with the length of the nanowires, nanowire bundles were assembled in the wells.

1. Introduction

The self-assembly behavior of colloidal particles is controlled by several competing forces. Gravity, Brownian motion, electrostatic attraction and repulsion, capillary effects, and dispersion forces all contribute to the equilibrium (and non-equilibrium) structures formed from particles. In order to form a well-ordered structure, one must generally begin with uniform particles. Colloids formed from silica,[1] metals,[2] and a number of polymers[3] can be used to form two- and three-dimensional ordered structures, termed “colloidal crystals”. Most ordered three-dimensional structures of this type have been formed by the concentration of electrostatically charged spheres, and ordered two-dimensional structures have been formed by harnessing capillary forces as liquid-dispersed particles are pulled towards an evaporation front.[4-6]

The assembly behavior of larger particles (> 5 μm) had not been explored until recently. Mechanical forces have been used to organize millimeter-scale objects on wafer surfaces.[7] Whitesides et al. have published a series of papers on the self-assembly of millimeter-scale objects at two-dimensional liquid–liquid interfaces,[8] and in solution to form three-dimensional crystals and circuits.[9] These objects reach minimum energy conformations by minimizing the meniscus curvature between the particles at the interface between the liquids. Howe and co-workers have used a similar effect for fluidic self-assembly, through which a photocurable polymer was coated onto 150 μm² metal particles, and these objects were assembled onto a flat patterned surface using capillary forces.[10] Recently, Whitesides et al. published a report in which 10 μm polyhedral metal plates have been organized into extended organized three-dimensional structures using capillary interactions, followed by cross-linking with a photocurable adhesive.[11] This report was the first demonstration of a three-dimensional organized structure composed of objects of in this size regime.

Some alignment and assembly experiments have been done on anisotropic particles. Theoretical treatments of rod packings have focused on possible close-packed structures with spheres,[12] and the structures of open networks.[13] Template-based nickel nanowires were aligned in a magnetic field.[14] The phase diagram for the packing of filamentous bacteriophage fd viruses with different concentrations of polymer spheres was mapped.[15]

Although a great deal of work has been published on the self-assembly of nanoscale colloids and of particles larger than about 10 μm, to date the assembly behavior of micrometer-scale metallic particles is largely unexplored. This is a physically interesting size regime because gravitational forces (which are less significant with smaller objects) and non-covalent surface interactions (which are operative but less important on larger length scales) are comparable in strength. For this reason, particle behavior must be analyzed at a fundamental level, and practical problems, such as the handling of materials of micrometer size, must be solved. This paper will focus primarily on observations of the attractive and repulsive electrostatic interactions between functionalized nanowires and planar surfaces. Included in this study is the use of gold-patterned silica surfaces, and surfaces with topographic relief patterns, which confine particles to specific locations.

For this work we used template-derived nanowires grown using the methods described by Martin and Moskovits.[16,17] In this approach, metals are deposited electrochemically inside of a porous membrane. The metal plating solution can be changed after each deposition step in order to generate multi-metal striped wires.[18] The resulting particles are rod-shaped with the diameter determined by the template, and the length determined by the total charge passed (see Experimental).[18,19] In order to allow easy visualization by optical microscopy, relatively large gold nanowires (average diameter of 350 nm) were used. The average length of the wires used to study planar surface interactions was 3 μm, and 6 μm wires were used in studies of wire assembly in topographic relief patterns.

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2. Results and Discussion

2.1. Sample Preparation

The sedimentation behavior of dense metallic particles presented difficulties in these studies, and several methods were developed to circumvent these complications. Modification of the surface charge by derivatization with self-assembled monolayers (SAMs) allowed the particles to be more easily resuspended, but this treatment did not prevent sedimentation. Particle aggregation was not observed to any appreciable extent before or after derivatization with mercaptoethylsulfonic acid. By stirring or agitating the nanowire solution, sedimentation could be minimized, but particle–surface impacts occurred with increased velocity. This resulted in particles that were bound to the wafer, presumably through dispersion forces between the highly polarizable metal surfaces. These non-specific interactions made the analysis of the resulting particle–wafer interactions difficult. A gentle way to reduce gravitational settling effects is the use of a tumbler cell.[20] By continually rotating a container containing the particles and wafer, a time-averaged zero-gravity environment is obtained. However, particles can bind to the surface of the tumbler cell unless the surface chemistry is carefully controlled. Over extended periods of time (>1 h), all surfaces become evenly coated within the cell. While these methods have proven useful for quantitative comparisons of particle coverage,[21] they do not allow for real-time studies of particle–surface interactions. For the experiments presented here, a nanowire solution was simply spread over a wafer surface dropwise and examined under a high power optical microscope. Although the droplet curvature distorted the image, this effect was minimal at the center of the droplet and was less apparent with larger droplet volumes.

The methods used for rinsing a surface were immersion in a clean bath, agitation in a bath, and spray washing. Agitation in a water bath and spray rinsing are both acceptable means of rinsing a surface as long as they can be done in a reproducible manner. However, a great deal of practice is required before one can use these methods to test nanowire–wafer interactions, since both methods can generate forces strong enough to remove specifically bound particles from surfaces. Capillary forces can be used to remove unbound particles from a surface as the surface is pulled through a liquid–air interface. As a wafer is lifted through the liquid–air interface, the particles are whisked from the wafer into the solution due to the strong capillary forces at the air–water interface, similar to the forces used to order two-dimensional colloidal crystals.[22]

2.2. Cyan/Magenta/Yellow Composite Images

One of the problems in understanding particle assembly is to extract dynamical information from a series of frames or still images. In order to differentiate particles in motion from immobilized particles, composite false color images were generated. These images were constructed by digitally multiplying three still images, each designated a color (cyan, magenta, or yellow), and each taken sequentially from the same location on a planar surface. In digital multiplication, cyan × magenta × yellow = black. Therefore, particles that have not moved in the time between the sequential images appear black, whereas particles in motion appear in different locations as all three colors. If overlap occurs between particles in sequential images, then additional colors result. The color code provides a means of tracking the motion of large numbers of individual particles, e.g., into and out of wells on a topographically patterned surface. This type of image is useful for understanding particle motion and adhesion, and will be called a cyan/magenta/yellow (CMY) composite image.[23]

2.3. Repulsive Interactions

Nanowires derivatized with mercaptoethylsulfonic acid (MESA) were examined on MESA-derivatized wafers, in order to study the behavior of nanowires that were electrostatically repelled from the planar surface. After a solution of suspended nanowires was spread on the surface, the particles were allowed to settle for 30 min. After this time, the wafer was examined under a microscope. 99+% of the particles in the CMY image were mobile on the wafer surface. Figure 1a is a bright-field micrograph of a 1.2×10⁻⁷ cm² area of the wafer surface. Figure 1b is a CMY composite image of the same region of the wafer, with a frame time-lapse of approximately 30 s. The lack of overlap of the particles between images resulted in an array of colors in the composite image. The motion of the particles is due to Brownian motion, resulting in

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Fig. 1. Mercaptoethylsulfonic acid (MESA) derivatized gold nanowires dispersed on a MESA-derivatized surface. a) Bright-field image. b) CMY composite image made from three images taken sequentially at the same location on the surface. Color indicates movement of particles on the surface. Scale bar = 50 μm.
a diffusion rate of approximately 0.5 μm² s⁻¹ at ambient temperature. These nanowires remained mobile on the surface for > 6 h. A small fraction (∼1 %) of the nanowires aggregated at the surface, and became immobile. When rinsed, all mobile nanowires were eventually removed from the surface.

Although efforts were made to keep contaminants to a minimum, these experiments were conducted on an open bench in the laboratory, so airborne dust particles could not be avoided. When they settled on the surface, these particles generally possessed a static charge. In some locations on the surface, nanowires were repelled from a small dust particle. An example of this behavior is shown Figure 2a. One can infer from the surface chemistry of the nanowires that this dust particle was negatively charged, and that charge repulsion was effective over distances of about 20 μm under these conditions. Positively charged dust particles (which were far less abundant than negatively charged dust) attracted nearby mobile nanowires (Fig. 2b). These effects were only observed on surfaces on which the particles were mobile.

Interessingly, the repulsion between negatively charged dust particles and nanowires extends far beyond the expected length scale of electrostatic interactions this solution.⁴ The Debye screening length, \( r_D \), in an electrolyte solution is given by Equation 1,

\[ r_D = \sqrt{\frac{eRT}{2\rho F^2I}} \]  

where \( e \) is the dielectric constant, \( \rho \) is the density of the fluid, \( I \) is the ionic strength, \( F \) the Faraday constant, \( R \) the gas constant, and \( T \) the absolute temperature. At 298 K in water (\( \epsilon = 78.54 \)), Equation 2 approximates Equation 1.

\[ r_D = 0.32 \sqrt{\frac{eRT}{2\rho F^2I}} \]  

For a suspension of \( 10^6 \) nanowires mL⁻¹ (3 μm × 350 nm), one expects at monolayer coverage (about \( 10^{10} \) mol cm⁻²) a SAM concentration of about \( 3 \times 10^{-7} \) M. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis of a concentrated sample containing approximately \( 10^6 \) nanowires per mL gave concentrations of S and Na of \( 1.1 \times 10^{-5} \) and \( 2.9 \times 10^{-6} \) M, respectively. Recalling that each MESA molecule contains two S atoms, the ICP-AES analysis results are consistent with approximately monolayer coverage. Interestingly, the S to Na ratio is greater than 2, although it was found to be 2.0 for a sample of the sodium salt of MESA analyzed in the same way. This suggests that some of the sulfonate groups on the nanowires are charge-compensated by positive image charges or possibly by adsorbed protons, rather than by Na⁺ counterions. For the \( 10^6 \) nanowire per mL samples used in the microscopy experiments, one can calculate \( r_D \approx 800 \) nm using the analytical [Na⁺] concentration and Equation 2. The surprisingly long-range interaction between particles evident in Figure 2a must represent a balance between the entropy-driven filling of the void space with nanowires and the weak electrostatic repulsion between charged particles separated by many times the Debye length.

2.4. Attractive Interactions

MESA-derivatized nanowires dropped onto wafers derivatized with 2-mercaptoethylamine (MEA) represented the opposite scenario from the MESA nanowire–MESA substrate experiment. In this case, the nanowires appeared to be immobilized upon contact with the wafer. This was in dramatic contrast to the repulsive experiment. However, this experiment was complicated by the fact that the contact angle of the MEA SAM on the wafer (approximately 70°) was greater than that for MESA (approximately 20°). Therefore, hydrophobic forces could be partly responsible for nanowire adhesion to the wafer surface. To ensure that this was not the case, a polyelectrolyte bilayer was deposited on a SAM of MEA on Au, consisting of one layer of poly(styrenesulfonate, sodium salt) (PSS), capped with one layer of poly(allylamine hydrochloride) (PAH). The PAH-derivatized surface had a contact angle comparable to that of the MESA-derivatized surface, and it possessed a positive surface excess charge. MESA-derivatized particles bound strongly to PAH-derivatized surfaces, indicating that this interaction is not merely a function of the contact angle. The interactions of MESA-derivatized particles with a PAH-derivatized surface are shown in Figure 3. The black color of particles in the CMY composite with a 30 s frame time lapse (Fig. 3b), shows there is essentially no particle motion on the timescale of the sequential images.

The coverage of particles on the surface for these attractive interactions is a function of the initial concentration of the par-
particles in solution and the area of the surface covered by that solution. Three dilutions of MESA-derivatized nanowires were dispersed on MEA-derivatized surfaces, and were followed in each case by an interfacial rinse. Table 1 summarizes the results of this experiment. The number of bound nanowires is directly proportional to the initial concentration of nanowires in the suspension. The number of bound nanowires in every case is approximately 40% of the number of nanowires released from the membrane. This discrepancy is most likely due to losses during centrifuge/wash cycles. This indicates that the attractive electrostatic interaction results in a high probability of nanowire “capture” by the oppositely charged surface. In the case of nanowires settling on a surface, this capture rate is dependent on the settling rate from solution.

Table 1. Adhesion of MESA-derivatized particles to MEA-derivatized gold.

<table>
<thead>
<tr>
<th>Nanowires dispersed in solution (theoretical)</th>
<th>Measured nanowires on surface [cm⁻²]</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 x 10⁶</td>
<td>4.5 x 10⁴</td>
<td>38%</td>
</tr>
<tr>
<td>1.2 x 10⁷</td>
<td>4.8 x 10⁴</td>
<td>40%</td>
</tr>
</tbody>
</table>

2.5. Covalent Interactions Through Dithiol Coupling Chemistry

Covalent interactions in the form of thiolate bonds between the wafer surface and nanowires were examined. As one would expect, when 1,4-butanedithiol is present at the wafer surface, the nanowires bind tightly to this surface. This process occurred as the particles made contact with the surface, and no motion was observed after the particles had settled. The particles bound in this way were resistant to a few seconds of ultrasonic agitation. The strength of these interactions is not surprising, since dithiols have been known to couple colloids strongly to surfaces. This coupling chemistry is useful as an “adhesive”, but it is far too strong to allow ordered structures to develop. Natan et al. have shown that the sticking probability for gold colloids approaching a dithiol-functionalized surface is approximately unity, indicating that this process is mass transfer controlled. Without reversible interactions, the structure resulting from interactions between the particles and the surface is simply a map of the collisions of the particles with the surface, similar to the electrostatically attracted particles.

2.6. Self-Assembly of Nanowires on Patterned Surfaces

Patterned surfaces represent a new challenge for self-assembly experiments. Multiple materials at a surface offer the possibility to orthogonally self-assemble functional groups on discrete sections of a surface. However, as the derivatization scheme becomes more complex, cross-contamination between functional groups becomes increasingly likely. Primarily, gold patterns on silicon/silicon dioxide and gold/divinylsiloxane-bis(benzocyclobutene) (BCB) surfaces were explored, since these were easily obtained using photolithographic techniques.

The surface of silicon, when freshly treated with an oxidizing acid, consists of hydrated silanol groups that are extremely hydrophilic. Nanowires coated with a hydrophilic SAM do not interact with this surface. This effect can be used to derivatize gold patterns on a freshly cleaned silicon surface selectively by forming a SAM on the gold pattern that is attractive to the SAM on the nanowires. The simplest interaction pair is the electrostatic interaction between MESA-coated nanowires and MEA-coated gold features. Figure 4 is an optical micrograph depicting this interaction. Figure 4a is a bright-field image at 200x magnification, and Figure 4b is a CMY composite of three images taken sequentially at one-minute intervals from the same region of the surface. The CMY composite clearly shows that the particles on the gold sections of the pattern are immobile over the timescale of the measurement, whereas the particles on the silicon oxide surface move freely. This method can be used to selectively bond particles to portions of a surface, but the particles are not oriented in any specific direction. Rather, the particles remain in the orientation that was adopted upon settling onto the surface, just as in the case for MESA–MEA interactions on a homogeneous gold surface.

When the patterned wafer containing bound nanowires was rinsed by passage through a water–air interface, the mobile particles were removed from the SiO₂, while the particles bound to the gold pattern remained. Figure 5 shows two dark-field micrographs of the wafer after this rinsing procedure. The density of the nanowires on the gold pattern is similar to the density obtained on a planar surface with the same concentration of nanowires.
similar to that recently demonstrated by Xia and co-workers for assembly of small collections of spherical objects in circular depressions on surfaces.\(^{[20]}\) Topographical features, here oblong wells in the surface, were created using photolithography. Each well in the array had dimensions commensurate with a raft-like group of nanowires, \(4 \mu m \times 8 \mu m \times 600 \text{ nm}\) deep. The upper surface was the BCB polymer. The bottoms of the wells were thermally evaporated gold. This differentiation of the surface materials allows a built-in flexibility in surface chemistries. In this case, both the BCB and gold surfaces were rendered hydrophilic, the BCB by oxygen plasma oxidation, and the gold by derivatization with MESA. Gold particles were also derivatized with MESA, making both the particle–particle and surface–particle interactions repulsive. When the nanowire solution was dispersed onto the patterned surface, the nanowires settled and were mobile, as they were on a homogeneously derivatized MESA surface. As the nanowires moved across the BCB surface, they encountered the wells. Under the influence of gravity, the nanowires fell to the bottom and were trapped there. Because the well bottom was repulsive to the nanowires, they could move within a well (as long as it was only partially occupied), but did not possess sufficient energy to escape. Figure 6a, a bright-field image, shows nanowires on the BCB surface and trapped in wells. As can be seen in the CMY composite, Figure 6b, the particles in the wells are mobile yet trapped, while the nanowires on the BCB surface are free to move (CMY composite taken at 1 min intervals). The mobility in a confined space necessitates a stepwise addition of nanowires to the wells. Initially, as a single particle is trapped, it has the greatest freedom of motion. As other wires enter the well, the freedom of motion is decreased due to crowding in the limited space. Over time, the trapped wires, which still experience mutual repulsion, can move relative to each other and arrive at an approximate energy minimum. Figure 6c shows that surface wells may be filled completely with few extra particles remaining on the surface. Induced by the confined geometry of the wells and the crowding of the anisotropic particles, the ordered rafts of nanowires resemble the smectic phase found in liquid crystals.

### 3. Conclusions

The CMY images reveal differences in nanowire mobility that depend on electrostatic interactions and gravitational forces. While nanoscale colloidal particles can respond rapidly to weak chemical interactions at their surface, the \(350 \text{ nm}\) diameter, 3–6 \(\mu m\) long nanowires used here are much more massive, and they therefore respond much more slowly to weak forces. The particles used in these experiments can be considered a suspension, rather than a colloid. Previous experiments have shown that upon sedimentation, unstable (attractive) suspensions result in open porous structures rather than the densely packed arrays formed from stable (repulsive) suspensions.\(^{[27]}\) Electrostatic forces are powerful ways to bind particles to a surface, but these forces are strong only within the Debye screening length. For particles suspended in dilute aque-
ous electrolytes, this is a small distance compared to the length of the particle. The experimental procedures described here lay some groundwork for the analysis of the equilibrium structures of sedimented, charged rod-shaped particles. By allowing negatively charged nanowires to settle onto wafers, the interaction strength could be modulated by changing the density of charged groups on the particle (adjustable using mixed monolayers), the particle length, and the particle concentration. To our knowledge, measurements of this type have not previously been made for particles of this size.

The analysis of the results obtained from particle assembly experiments is far from simple. A particle can stick to a surface through van der Waals forces, solvent exclusion effects, and electrostatic effects, as well as less powerful forces such as the hydrogen bonds of hybridized DNA. The question becomes not “did the particles interact with the surface?” but rather, “how strongly did the particles interact with the surface?” When this question is answered, one can interpret data in the context of interaction energies and dynamical models to test whether the patterns observed are consistent with the anticipated forces. There are a number of ways by which this problem might be approached. We can think of the energy required to break or disrupt attractive interactions as another form of bath energy, with an energy range different from a simple thermal bath. A low-frequency oscillator (a loudspeaker) might be the appropriate sources of energy for some of these interactions. This device may be positioned within a liquid chamber on a microscope stage, and particle-surface interactions could be monitored as a function of the oscillation energy (adjusted by frequency and amplitude). We hope to address some of these questions in the future, now that techniques for visualizing and controlling the surface mobility of nanowires have been developed.

4. Experimental

Gold nanowires were prepared as described previously [18]. Briefly, one side of an alumina filter membrane (Whatman) containing 350 nm diameter internal pores was coated with 150 nm of thermally evaporated silver. This backing layer was used as an electrode onto which silver (from Silver 1025, purchased from Technic, Inc.) was deposited. An initial deposition step at 5 mA/cm² for one minute served to fill any pinholes in the evaporated silver. The membrane was inverted in the plating cell, and silver was again deposited at 2 mA/cm² for 30 min to form silver posts onto which gold was subsequently electrodeposited. Gold (Orotompe 24, purchased from Technic, Inc.) was electrodeposited at a rate of 0.55 mA/cm² for 1 h (for 3 μm particles) or 2 h (for 6 μm particles). The silver was dissolved in 50 % nitric acid, and the alumina membrane was then dissolved in aqueous sodium hydroxide to release the gold nanowires. These particles were sedimented by centrifugation, and the supernatant was removed by pipette. Deionized water was added, the particles were resuspended by ultrasonication, and the rinse process was repeated. After four cycles, the nanowires were ready for derivatization with self-assembled monolayers (SAMs).

The term “wafer” is used in this paper to represent any planar surface onto which nanowires are assembled. For unpatterned surfaces, glass microscope slides coated with 100 nm of thermally evaporated gold on a 5 nm chromium adhesion layer were used (purchased from EMF). These slides were cleaned by soaking them in piranha solution (3:1 conc. sulfuric acid/hydrogen peroxide. Danger - reacts violently with organic matter.) for 1 min, followed by a deionized water rinse. Patterned wafers were formed by photolithographically patterning photoresist on a silicon wafer. Thermal evaporation of 100 nm of gold on a 5 nm chromium adhesion layer and subsequent lift-off of the resist resulted in gold features on the silicon wafer. These wafers were cleaned using a similar piranha/water rinse treatment. Topographically patterned wafers were formed by similar means. Briefly, Cr/Au was evaporated directly onto a Si wafer, divinylsilsloxane-bis(benzocyclobutene) (BCB) was spin-coated onto the Au, and the well array pattern was formed in a top layer of photoresist. The pattern was transferred to the BCB layer by dry etching with CF₄/oxygen plasma, and the remaining photoresist was removed with acetone to generate the array of surface wells. The BCB outer surface was then rendered hydrophilic by oxidation with oxygen plasma.

SAMs were formed on nanowires by suspending the nanowires in a 1 mM solution of mercaptoethanesulfonic acid sodium salt (MESA) for 1 h. The nanowires were then rinsed four times with water using centrifuge/wash cycles. Self-assembled monolayers on gold-coated wafers were formed by immersing the surface in a 1 mM solution of the appropriate thiol [19]. The coverage of MESA on the nanowires was determined by analyzing suspensions for Au, S, and Na using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, on a Jarrell-Ashe Model 61E spectrometer) for Na and S. Nanowire suspensions were digested in 0.5 mL aqua regia (3:1 conc. HCl/HNO₃) and diluted with doubly deionized water for these experiments.

The concentration of nanowires was calculated by dissolving a 3.14 cm² alumina membrane containing nanowires in 7.8 x 10⁵ pores cm⁻² in sodium hydroxide. When the particles were rinsed and diluted to a volume of 1 mL, this yielded a solution containing approximately 1.4 x 10⁹ nanowires. This solution was further diluted to the desired concentration. Particles were dispersed on a surface by depositing 100 μL of an aqueous solution containing 10⁵ nanowires per mL onto a 1 cm² wafer. This slide was immediately transferred to the stage of an optical microscope, and the solution was observed as the nanowires settled on to the surface. When the particles had completely settled (> 5 min), the slide was rinsed by
a capillary rinsing procedure. The wafer was held vertically above a bath of water and immersed and withdrawn from this bath at a rate of one cycle per second. The motion was restricted to the vertical direction to minimize other forms of agitation. This process was repeated for 20–40 cycles. Generally, the water bath was changed after 30 cycles to reduce contamination of the surface by previously removed nanowires.

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[19] Gold-coated wafers were immersed in a 1 M solution of mercaptoethyl-sulfonic acid, mercaptoethylamine (MEA), or 1,4-butanedithiol (in ethanol) for 1 h. Polyelectrolyte multilayers were formed on the surface by alternately dipping a wafer into 20 mM (by monomer) aqueous solutions of poly(styryl sulfonate, sodium salt) and poly(allylamine hydrochloride) for 15 min per cycle with a water rinse between each exposure.
[23] While we are not aware of other use of CMY images in the scientific literature, we note that similar composite images were used by early photographer S. M. Prokudin-Gorski to generate color projections from black-and-white plates (Robert H. Allshouse, Photographs for the Tsar: The Pioneering Color Photography of Sergei Mikhailovich Prokudin-Gorski, Dial Press, New York 1980).