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Lejun Qi a, Peter H. McMurry b, David J. Norris a & Steven L. Girshick b

a Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, USA
b Department of Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota, USA

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Micropattern Deposition of Colloidal Semiconductor Nanocrystals by Aerodynamic Focusing

Lejun Qi,1 Peter H. McMurry,2 David J. Norris,1 and Steven L. Girshick2

1Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, USA
2Department of Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota, USA

We report the use of aerodynamic lenses to deposit micropatterns of colloidal semiconductor nanocrystals (or quantum dots). CdSe and CdSe/ZnS core/shell nanocrystals, with core diameters of 3.5–5 nm, were dispersed in hexane and then nebulized to generate agglomerates a few tens of nm in diameter, consisting of hundreds of nanocrystals. These agglomerates were then focused aerodynamically by a lens system. Microscale towers, lines, and patterns were deposited on thin sapphire plates and silicon wafers. The heights and widths of the deposits were adjustable by varying the experimental parameters. Line widths below 10 µm were achieved by liquid jetting driven by an electric field and utilizing fine micro-nozzles. In both micropenning and e-jet printing, the deposits consist of closely packed nanocrystals embedded in the organic matrices. This approach, which is not restricted to semiconductor nanocrystals, provides an alternative means for the deposition of microscale patterns of colloidal nanoparticles.

INTRODUCTION

Semiconductor nanocrystals (NCs) exhibit electrical and optical properties that are different from those of bulk materials. Because these properties can also be easily tailored through choice of growth conditions, they are potentially useful for various optoelectronic devices, including light-emitting diodes (Colvin et al. 1994; Steckel et al. 2003), photodetectors (Böberl et al. 2007; Konstantatos et al. 2006; Oertel et al. 2005), and solar cells (Gur et al. 2005; Huynh et al. 2002; Leschkies et al. 2007; Liu and Kamat 1993; Robel et al. 2006). For some of these devices, the deposition of NC assemblies with controlled patterns is an essential step in the fabrication process. Common methods include drop casting (Murray et al. 2001), spin coating (Finlayson et al. 2000; Snee et al. 2005), electrophoretic deposition (Islam and Herman 2002), and mist deposition (Zhu et al. 2008). Direct-write methods such as ink-jet printing (Böberl et al. 2007; Tekin et al. 2007) are also attractive because they avoid mask screening, lithography, and pre-patterning of the substrate and can therefore simplify micropatterning and allow inexpensive and rapid prototyping (Chrisey 2000).

Several direct-write techniques have been reported for producing 10 µm scale structures of colloidal nanomaterials. Micropenning has been used to write high resolution metallic patterns. This approach utilizes micro-capillary technology and a proprietary positive displacement method to pump flowable metallic particle paste onto a surface (Suzuki et al. 1997). More recently, electrohydrodynamic jet (e-jet) printing was used to deposit lines consisting of silicon particles or single-walled carbon nanotubes (Park et al. 2007). In this case, high resolution was achieved by liquid jetting driven by an electric field and utilizing fine micro-nozzles. In both micropenning and e-jet printing, the line widths of the deposits are approximately equal to the exit diameter of the nozzle or capillary. For example, in e-jet printing sub-10 µm features have been deposited using sub-10-µm nozzle tips (Park et al. 2007). However, such fine nozzles can be prone to clogging and can be less durable than larger ones.

Moreover, in the case of e-jet printing or other electrostatic aerosolization methods, adequate electrical conductivity is required to achieve a stable jet mode so as to atomize NC dispersions steadily. Non-polar solvents are poorly conductive, but achieving dispersions of NCs in polar solvents, while still maintaining NC fluorescence, is typically achieved after synthesis by further manipulation of the NC surface chemistry, which adds complexity to the process.
To avoid these issues, aerosol jet printers have been developed that employ a stream of sheath gas in the nozzle to deposit ultrasonically aerosolized droplets. Using a metallic ink, this technique can write metal interconnects for electronic applications. With a nozzle exit diameter of 100 μm, line widths of 14 μm have been obtained, indicating focusing. Even finer line widths could be obtained with a 50 μm nozzle (Mette et al. 2007).

However, compared to the direct-write techniques discussed above, nanoparticle deposition using aerodynamic lenses has several potential advantages (Di Fonzo et al. 2000). It requires neither a sheath gas nor micro-nozzles to achieve high (∼10 μm) resolution. Aerodynamic lenses consist of easily manufactured thin metal plates with orifices that are greater than a millimeter in diameter. An aerodynamic lens assembly can also be readily incorporated into high vacuum systems commonly used in microelectronics fabrication and take advantage of the pressure drop from ambient to the chamber to deposit the NCs. Designing and evaluating an aerodynamic lens system can be accomplished with a simple Excel-based tool, Aerodynamic Lens Calculator (Wang and McMurry 2006b). After inputting parameters including particle properties, carrier gas properties, upstream pressure, aerosol flow rate, the number of lenses, and the deposition chamber pressure, either an optimal lens system design or the performance of an existing lens system can be determined.

Aerodynamic lenses are widely used to generate particle beams for aerosol characterization. In at least one case—a study of elastic light scattering from SiO2 particles in the diameter range 100–240 nm—aerodynamic lenses were used to generate focused beams of colloidal particles that were transferred to the lenses from liquid dispersions by means of a nebulizer (Shu et al. 2006). Aerodynamic lenses were also previously used to deposit focused beams of ∼20 nm diameter Si and SiC nanoparticles onto Si substrates (Di Fonzo et al. 2000). The nanoparticles were extracted into the lens system directly from a plasma synthesis reactor. Needle-like “microtowers” were deposited on stationary substrates. Microscale lines and patterns were obtained by scanning the substrate across the focused particle beam.

It is not a priori obvious from this previous work that aerodynamic lenses can be used successfully to deposit colloidal semiconductor NCs for optoelectronic applications. The fluorescence wavelength of semiconductor NCs depends sensitively on their size, and for many materials fluorescence in the visible range requires particle diameters around or below 5 nm (Klimov 2004). While aerodynamic focusing has been demonstrated for particles down to 3 nm in diameter (Wang and McMurry 2006a), the \( d_p^{-2} \) dependence of Brownian diffusion coefficients, where \( d_p \) is particle diameter, causes particle beam widths to increase as particle diameter decreases, particularly in the sub-10-nm diameter regime. A second issue is that atomizing NC colloids to generate an aerosol consisting of single NCs may be prohibitively difficult, particularly if one considers that each NC must remain capped by a passivating surfactant (Klimov 2004). Third, particles that exit an aerodynamic lens assembly are strongly accelerated in the low-pressure environment required to maintain the focusing effect, and their impact velocity on a deposition substrate may equal several hundred m/s. To our knowledge no previous studies have assessed whether properties such as NC fluorescence would be retained in the deposit after such high-velocity impacts.

In this article, we report the first use, to our knowledge, of aerodynamic lenses to deposit focused beams of fluorescent colloidal NCs that are aerosolized from liquid dispersions. A key aspect of this work is that we found that it was not necessary to produce aerosolized single NCs. Instead, we achieved deposition of fluorescent deposits, with line widths of ∼10 μm, by focusing NC agglomerates, where each agglomerate was a few tens of nm in diameter and contained a few hundred NCs. This approach avoids the potential problems noted above with regard to aerosolization and focusing of single, surface-passivated NCs, while producing a result that is likely superior from the application viewpoint, because of the narrower beam widths associated with aerodynamic focusing of particles that are a few tens of nm rather than a few nm in diameter. The resulting deposits exhibited robust fluorescence, demonstrating that this property survives the high-velocity impact, estimated at 400–500 m/s.

In this article, we describe the process of nebulizing and focusing colloidal CdSe NCs and present representative results. A detailed study of NC agglomerate impact and deposit structure, currently in progress, will be reported in a subsequent publication.

**EXPERIMENTAL**

**Aerosolization of Colloidal Nanocrystal Dispersion**

Our process begins with luminescent, nearly monodisperse CdSe NCs synthesized according to standard methods (Peng and Peng 2001; Reiss et al. 2002). To estimate the NC size, we used the lowest energy absorption peak (Yu et al. 2003). On some of our CdSe samples, a thin ZnS shell was grown to increase their fluorescence efficiency to characterize the deposited patterns optically (Hines and Guyot-Sionnest 1996). All of the NCs were capped with tri-\( n \)-octyolphosphine oxide (TOPO) and dispersed in hexane. Before aerosolization, the number concentration was set to about \( 2 \times 10^{13} \) NCs/cm\(^3\) by adjusting the optical absorbance at 350 nm (Klimov et al. 1999; Leatherdale et al. 2002). A homemade pneumatic nebulizer was then used to atomize the NC dispersion (see Figure 1). Helium gas was injected into the nebulizer at a pressure of 240 kPa to generate a continuous output of droplets about 3 μm in diameter, each of which contained ∼300 NCs. After nebulization, the hexane quickly evaporated and the aerosol was fed through a diffusion dryer filled with freshly activated carbon powder to remove the hexane vapor. After this process, agglomerates of NCs were obtained.

The size distribution of the agglomerates exiting the dryer was measured with a scanning mobility particle sizer (SMPS)
FIG. 1. Schematic of nanocrystal aerosolization. Red lines indicate the direction of gas flow. Dry helium gas is injected as a carrier gas into a home-made nebulizer. Aerosol droplets, \( \sim 3 \mu m \) in diameter, are created from a dispersion of CdSe nanocrystals in hexane. After the hexane evaporates, its vapor is removed by a diffusion dryer containing freshly activated carbon powder. Agglomerates consisting of \( \sim 300 \) nanocrystals are then sent to the lens assembly.

(McMurry 2000; Wang and Flagan 1990). A typical result, shown in Figure 2, exhibits a distribution that peaks at a diameter of 35 nm. In other experiments, the peak diameter varied from 30 to 40 nm depending on the concentration of free TOPO in the solution and the NC size. The CdSe NCs, which were 3.5 nm in diameter in this case, account for \( \sim 30\% \) of the agglomerate volume. The remaining \( \sim 70\% \) is presumably occupied by the residue from the aerosolized solution, including free surfactants and nonvolatile impurities.

Aerodynamic Focusing of Nanocrystal Agglomerates

These aerosolized agglomerates were then passed through a pressure-limiting orifice (200 \( \mu m \) diameter) and flushed into the stainless steel aerodynamic lens assembly. The detailed principles of aerodynamic lenses were discussed previously by Liu et al. (1995). As illustrated in Figure 3, the assembly consists of a series of center-collimated orifices, distributed in a tube, that create converging flow accelerations and diverging decelerations. Particles in the flow are inertially focused into a tight beam after passing through several orifices. The exit nozzle then accelerates them toward the substrate with minimized divergence angle. The pressure-limiting orifice controls the volumetric flow rate through the lens system, and the exit nozzle defines the lens operating pressure. Two important operating parameters, the pressure in front of the first lens and the pressure of the deposition chamber, are monitored respectively by pressure gauges \( P_1 \) and \( P_2 \) in Figure 3. The chamber is evacuated by a turbomolecular pump.

Using the Aerodynamic Lens Calculator and assuming a mass density of 2.0 g/cm\(^3\) for our agglomerates, we found that the lens assembly designed by Di Fonzo et al. (2000) was also suited to this study. Each lens was 0.3 mm thick with an orifice diameter of 2.26 mm. The exit nozzle had an inner diameter of 1.85 mm and the barrel of the lens assembly was sealed by a system of double o-rings into the deposition chamber. Because our agglomerates were in a size regime where diffusion broadens the beam formed by the aerodynamic lenses, we selected helium as the carrier gas to lessen this effect (Wang et al. 2005).

RESULTS

Microtower Deposition

Figure 4 demonstrates a sharp microtower that we deposited on a thin sapphire plate from agglomerates of CdSe/ZnS...
core/shell NCs. The substrate was located 2 mm downstream from the exit nozzle and held stationary for 10 min. As seen in the scanning electron microscopy (SEM) image of Figure 4a, the deposit consists of a sharp peak with a surrounding circular area hereafter referred to as the "tail region." The microtower has a height of 158 µm with a full width at half maximum (FWHM) of 27 µm, indicating a height/FWHM ratio of 5.85. The same deposit was also imaged under ultraviolet illumination with a fluorescence microscope (Figure 4b). Yellow-green photoluminescence was observed, consistent with the 3.7 nm CdSe cores that were used. This also indicates that the individual NCs remained passivated by the surfactants despite the high impact velocity, estimated at 400–500 m/s, on the sapphire plate. Both the SEM and fluorescence measurements show that the diameter of the entire deposited area (including the tail region) is around 400 µm. Considering the possibility of motion or diffusion of the agglomerates along the substrate after impact, the width of the focused agglomerate beam was likely less than the 400-µm diameter of the deposit. Moreover, because the beam is significantly smaller than the inner diameter of the exit nozzle (1.85 mm) and very few of the agglomerates are expected to be lost in the lens assembly according to the Aerodynamic Lens Calculator, clogging of the nozzle is not an issue.

**Microline Deposition**

To deposit patterns, the substrates were translated during deposition with a 3-axis computer-controlled motorized stage (Figure 3). While the speed of this stage was variable, for the depositions reported here we utilized a speed of 10 µm/s. Figure 5 shows a line deposited by scanning the stage back and forth five times across a silicon wafer. Similar lines were also formed on sapphire and glass substrates. After deposition, the substrate was fractured in liquid nitrogen. As seen in the SEM image of Figure 5a, with ten passes of the translation stage, the deposited line did not break with the substrate, resulting in a 130-µm-long cantilever suspended at the wafer edge. For this cantilever, only the central portion of the deposit remained; the surrounding thin tail region was removed with the substrate. The same effect was observed for lines deposited on glass slides. As with the microtower above, the line deposits also exhibited photoluminescence (Figure 5b).
FIG. 6. SEM cross-sectional images of lines deposited from 5 nm CdSe nanocrystals on thin glass slides. The substrate was passed (a) two and (b) six times through the beam at a speed of 10 \( \mu \text{m/s} \) while maintaining \( P_1 \) at 1100 Pa and \( P_2 \) at 1.3 Pa. The cross sections were obtained by fracturing the substrate perpendicular to the line in liquid nitrogen.

We also deposited lines with fewer passes of the translation stage. In this case, the deposits were thinner and cleaved with the substrate when we fractured the sample in liquid nitrogen. Thus, clean cross sections could be obtained. Figure 6 shows cross sectional SEM images of two lines deposited on thin glass slides. The conditions were identical except two deposition passes were used in Figure 6a, and six in Figure 6b. In both cases, the cross sections are seen to have a roughly triangular profile. For the two-pass line the height is 2.9 \( \mu \text{m} \) and the FWHM equals 9.4 \( \mu \text{m} \), while for the six-pass line the height is 7.0 \( \mu \text{m} \) and the FWHM equals 7.5 \( \mu \text{m} \). These results, as well as the microtower in Figure 4, illustrate the “self-sharpening” nature of focused particle beam deposition. The particle concentration in the focused beam at the nozzle exit is axisymmetrically Gaussian-distributed along the radial direction (Liu et al. 1995), resulting in the triangular cross sections seen in Figure 6.

**Photoluminescence Spectroscopy Characterization**

Figure 6 also indicates that the NCs are densely packed in the deposits without signs of porosity, at least at the resolution of the images. This is also consistent with photoluminescence spectra measured for the tower and line deposits from Figures 4 and 5. The maximum of the fluorescence was observed at 569 nm, while fluorescence from the same NCs peaked at 565 nm when they were dispersed in hexane (see Figure 7). The 4 nm red shift in the deposits is consistent with previous measurements on quantum dot solids (Kagan et al. 1996). Hence, we conclude that our tower and line deposits are solids consisting of closely packed NCs in an organic matrix.

The ability to pattern fluorescent NCs at specific locations can potentially have applications in creating active areas for devices such as light-emitting diodes or thin-film transistors. While we focused here on semiconductor NCs, our approach is generally applicable and should allow a variety of colloidal nanoparticles to be deposited. Thus, wires of conductive channels consisting of metallic nanoparticles could also be patterned and combined with semiconductor deposits.

**REFERENCES**


