Silicon and Germanium Nanocrystal Thin Films Prepared Using Innovative Nonaqueous Electrophoretic Deposition

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ABSTRACT

Universal Nanotech Corporation (UNC) has successfully developed a new process for creating thin films from colloids of size-specific silicon (Si) and germanium (Ge) nanocrystals (NCs). Raw Si and Ge NCs synthesized through UNC's proprietary continuous high-throughput production process (>100g/hr) were fabricated into thin films using nonaqueous electrophoretic deposition (EPD). We demonstrate that uniform and cohesive films ranging from 100nm - 1μm can be deposited onto a conductive substrate within a timeframe of 10s - 300s depending on desired film thickness. In this paper, we report for the first time physical characterization results of intrinsic Si and Ge NC thin films fabricated with EPD. Films were characterized through scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

Keywords: nanocrystal, nanoparticle, silicon, germanium, film

1 INTRODUCTION

As cost effective synthetic routes for producing large quantities of high purity size-specific nanoparticles become fully realized, the next challenge lies in fabricating devices that utilize the unique size-dependent optoelectronic properties inherent in quantum dot materials. The optoelectronic properties of semiconductor nanocrystals (NCs) have been rigorously researched and demonstrate desirable capabilities previously unattainable with bulk materials[1]. Harnessing semiconductor NC characteristics to advance the functionality of devices such as solar cells, supercapacitors, and rechargeable batteries, hinges upon creating a highly ordered cohesive film. Methods of semiconductor NC film deposition which have been comprehensively investigated include layer-by-layer dip coating[2], spin casting[3], and plasma enhanced chemical vapor deposition[4]. However, relatively little research has been reported to employ techniques of electrophoretic deposition (EPD). While aqueous EPD using chlorides of silicon and germanium has seen some attention[5], the voltages required to deposit pure silicon and germanium nanocrystals from a colloid surpass the 3 to 4 volt threshold above which the electrolysis of water occurs. However, recent investigation into the electrochemistry of nonaqueous solvents has made considerable progress through greater understanding of dynamic solvent effects on electrochemical processes[6]. This paper reports Universal Nanotech Corporation's initial characterization results of thin films fabricated from high-purity size-specific silicon and germanium nanocrystals using nonaqueous electrophoretic deposition.

2 EXPERIMENTAL METHODS

High-purity size-specific hydrogen terminated Si and Ge NCs (see Figures 1-6) produced by Universal Nanotech Corporation's proprietary process were suspended in a blend of nonaqueous solvents and ionic fluids to facilitate electrophoretic deposition onto a conductive substrate. A transparent conductive oxide substrate consisting of an indium tin oxide (ITO) layer on glass was used for all data presented in this paper. Parameters including voltage, current, fluid temperature, time, pH, and distance from the ITO substrate to the anodic electrode were varied and analyzed to determine optimal values needed to achieve desirable film characteristics. Nanocrystal concentrations in the fluid used for EPD were held constant throughout the experiments in order to minimize the amount of experimental variables.

Due to the large amount of interdependent variable experimental parameters and the substantial quantity of statistical data associated with optimizing parameters for desirable NC film qualities, a detailed description leading to how appropriate values were established is beyond the scope of this paper. Universal Nanotech Corporation has applied for patent protection covering the intellectual work which was required to design the NC film deposition process and are available to license for interested parties. For this reason, a generalized summary of a typical experiment will be given for conceptual purposes.

Indium tin oxide coated glass 3cm in length by 1cm in width ($3cm^2$) served as the working cathodic electrode and was placed into a mixture of nonaqueous solvents and ionic fluids with a specific known concentration of nanocrystals to be deposited. Approximately $1cm^2$ of ITO was submersed into the mixture. Next, an anode of an appropriate material was submerged at a specific distance from the ITO substrate. An external power source provided the necessary electric field to drive the NCs suspended in the colloid onto the cathodic ITO substrate. The process

was allowed to continue for a precise amount of time in order to achieve the desired film thickness. At the appropriate time, the ITO was removed from solution and characterized by scanning electron microscopy and energy dispersive X-ray spectroscopy. No additional materials or processes were applied to the film post deposition.

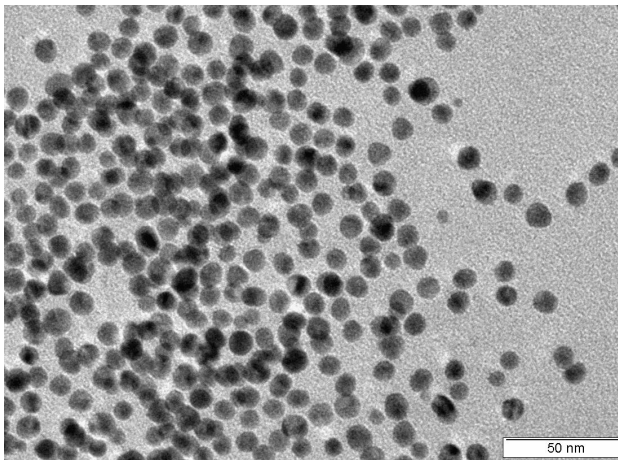


Figure 1.

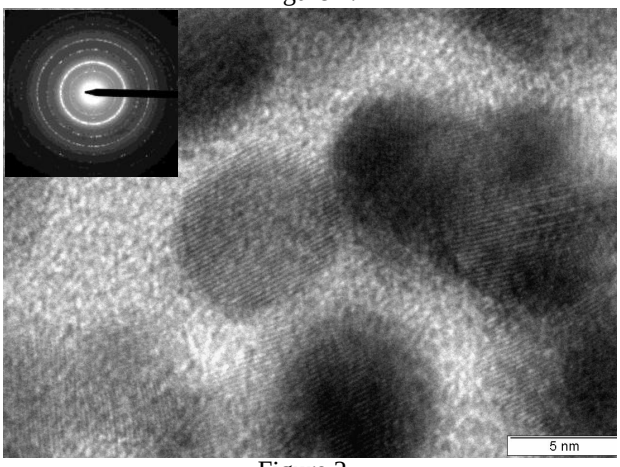


Figure 2.

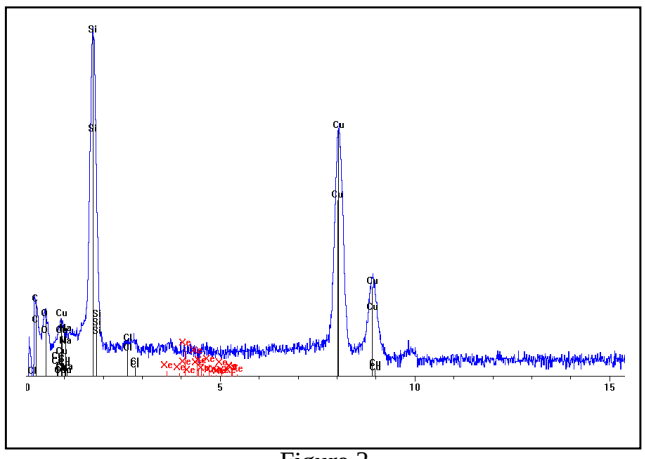
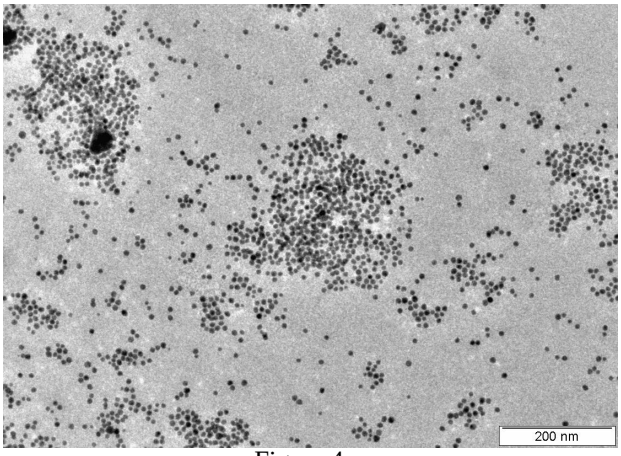


Figure 3.



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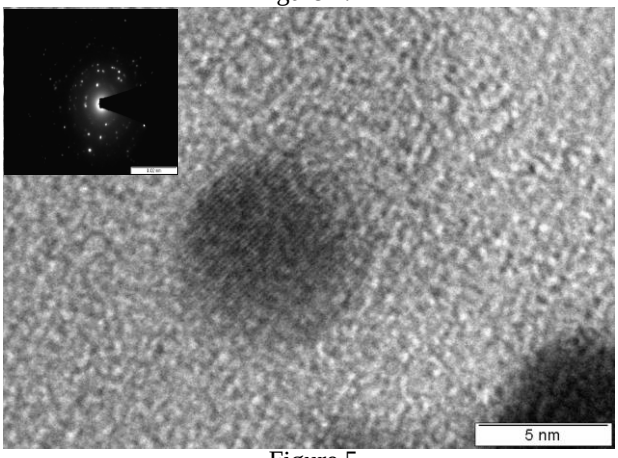

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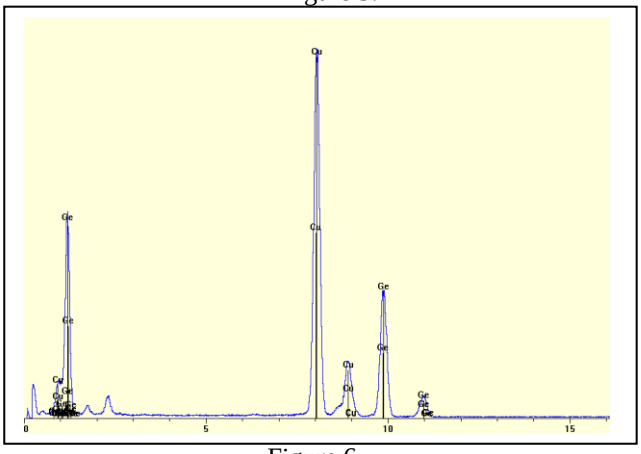

Figure 6.

Figure 1. TEM of 5nm Si NCs demonstrating monodispersity.
Figure 2. Hi-res 5nm Si NCs showing crystal lattice planes with spot diffraction pattern inset.
Figure 3. EDX of 5nm Si NCs. Copper and carbon peaks due to Ted Pella Carbon Type-B 200 Mesh Copper Grid.
Figure 4. TEM of 9nm Ge NCs demonstrating monodispersity.
Figure 5. Hi-res 5nm Ge NCs showing crystal lattice planes with spot diffraction pattern inset.
Figure 6. EDX of 9nm Ge NCs. Copper and carbon peaks due to Ted Pella Carbon Type-B 200 Mesh Copper Grid.

3 RESULTS AND DISCUSSION

Figures 7 & 8 show SEM images of 10nm Si NCs and 9nm Ge NC films respectively as a result of optimized experimental parameters. The SEM images and EDX data demonstrate that the EPD process deposited only elemental silicon and germanium from the nonaqueous solvent / ionic solution mixture. The images indicate nanocrystals are densely packed in a continuous film over the area of ITO submerged in the colloid. Lack of oxide present in the EDX spectroscopy suggests that the particle surface remained stabilized by hydrogen termination and good interparticle cohesion was obtained as a result of Van der Waals forces. Although the film could be easily scratched, the adhesive force between the nanocrystal film and the ITO layer was sufficient to remain intact when a strip of 3M Magic™ Scotch® tape was pressed onto the surface and removed.

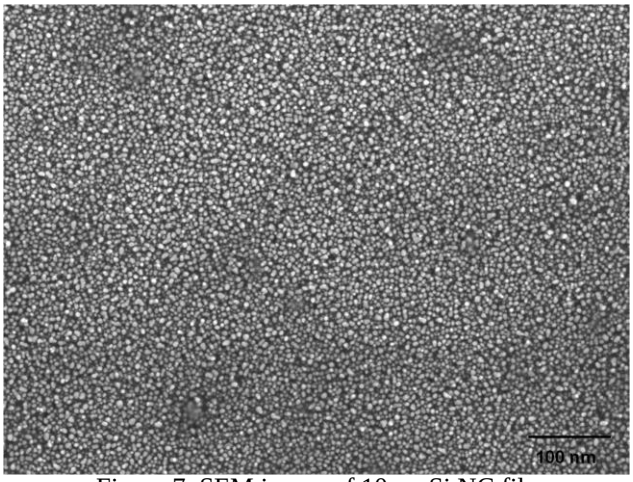

Figure 7. SEM image of 10nm Si NC film.

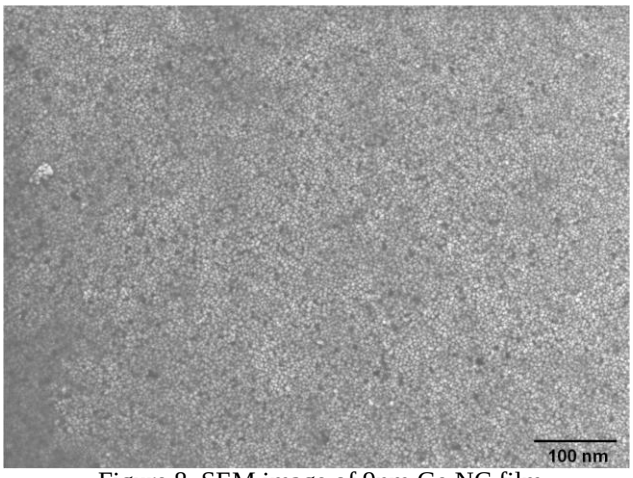

Figure 8. SEM image of 9nm Ge NC film.

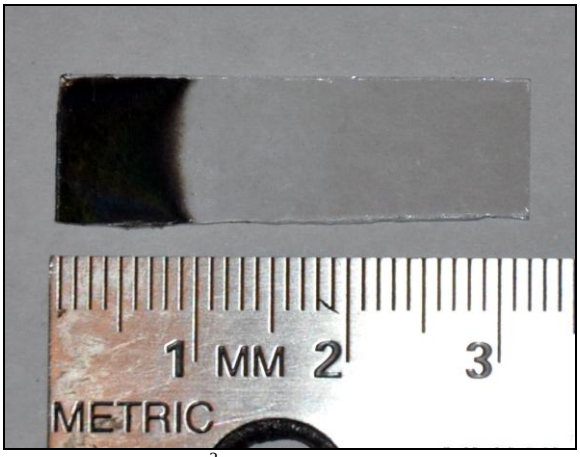

Figure 9. 1cm^2 Si NC film deposited on ITO.

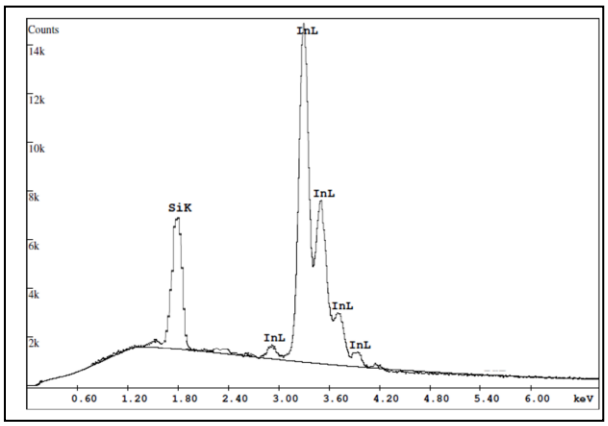

Figure 10. Energy dispersive X-ray (EDX) of 10nm Si NC Film. Data acquisition was initiated at 0.7 keV. Note that the peaks beyond 2.5 keV are due to indium.

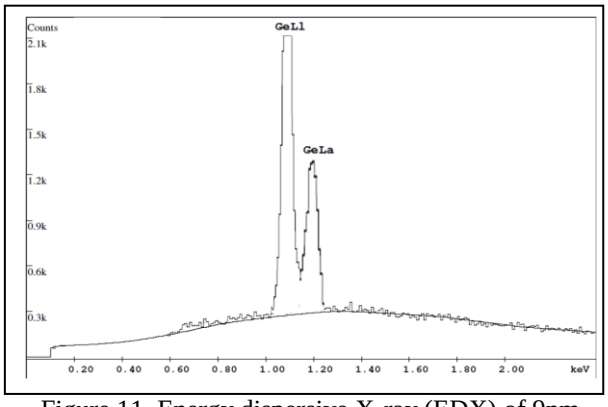

Figure 11. Energy dispersive X-ray (EDX) of 9nm Ge NC Film. Data acquisition was initiated at 0.6 keV and stopped at 2.5 keV just before indium peaks demonstrated in the above Si NC film EDX.

4 CONCLUSIONS

In this paper we demonstrate that electrophoretic deposition in nonaqueaous solvents can be used to create thin uniform cohesive nanocrystal films from a colloid. The films can be deposited within a timescale of 30s to 300s. Low cost high quality film deposition can be realized with basic equipment in a standard laboratory setting without specialized cost prohibitive apparatus such as an ultra clean environment, high vacuum, or plasma enhanced chemical vapor deposition chamber. Future experiments will focus on layering different size nanoparticles in specific sequences in effort to utilize the unique size dependent optoelectronic properties inherent in quantum dot materials. In parallel to this, the addition of metal contacts as well as incorporating p-type and n-type doped nanocrystals into the fundamental architecture of UNC thin film devices will be comprehensively researched.

With the low cost and efficient electrophoretic deposition process described in this paper and the capability to produce and maintain large in-house stocks of size-specific silicon and germanium nanocrystals, Universal Nanotech Corporation will continue to make rapid progress towards bringing a nanomaterial thin film device to fruition on a commercial scale.

5 REFERENCES

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