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1. Introduction

There are several applications that require a thin layer of nanoparticles that are spread uniformly and without agglomeration over a surface. Among these applications are carbon nanotube synthesis and the development of fuel cells, advanced sensors, and optoelectronic devices. There is a need for improved processes of forming these nanoparticles. Among the numerous methods that have been developed, pulsed laser ablation has proved (ElShall et al., 1995; Burr et al., 1997, Seraphin et al., 1997, Geohegan et al., 1998; Lowndes et al, 1998, Makimura et al., 1998; Becker et al., 1998; Lowndes et al., 1999; Makino et al., 1999; Link and El-Sayed, 2000; Mafune et al., 2000; Mafune et al., 2001; Ogawa et al., 2000; Tang et al., 2001; Ozawa et al., 2001; Hata et al., 2001; Barnes et al., 2002) to be especially effective because of the potential for congruent ablation, the ability to produce nanoparticles of high purity, the ability to deposit nanoparticles on room temperature substrates, and the relative simplicity of the process. One problem with conventional pulsed laser ablation is the observation that the deposited material, in addition to containing nanoparticles, also contains large, μm-sized particles. These are formed through a process denoted splashing (Ready, 1963), which occurs when a transient liquid layer is formed in the irradiated volume of the target; liquid droplets can be ejected from the target by the recoil pressure of the expanding gas on the transient liquid layer. Traditionally, splashing has been minimized (but not eliminated) by ablating very smooth targets or by using low laser energy densities. Target splashing is an issue in nanoparticle synthesis since the deposition of large particles within a field of nanoparticles makes it considerably more difficult to exploit the unique properties of isolated, non-agglomerated nanoparticles. Target splashing is also an issue because it represents material waste. There is, therefore, a need for a laser ablation process that further reduces or, ideally, eliminates splashing in nanoparticle synthesis. In addition, there is the further need for a process that minimizes nanoparticle agglomeration.

Presented here is a process, denoted Through Thin Film Ablation (TTFA), which enables the efficient synthesis of nanoparticles. TTFA, in addition to substantially reducing the probability of large particle splashing, also reduces significantly the problem of nanoparticle agglomeration. The TTFA process is based on irradiating a very thin layer of target material from the backside. The use of such a thin target allows one to reduce the thickness of the
liquid layer to such an extent that splashing of large particles is eliminated. Use of a very thin target has the added benefit of minimizing nanoparticle agglomeration. TTFA was originally developed as a method to synthesize transition metal nanoparticles for catalytic growth of single walled carbon nanotubes. The TTFA process has since been used to synthesize nanoparticles of several other materials including Fe (Murray and Shin, 2009), Pt (Petry, 2009; Tschopp et al., 2009), Ni, Ti, and Si. TTFA is illustrated here by presenting the results for Ag (Murray and Shin, 2008) nanoparticle formation.

2. Experimental

Nanoparticle synthesis by TTFA is carried out by ablating, from the backside, a very thin (10’s of nm) film of the selected nanoparticle material. Ablation is carried out in the presence of a background gas (typically Ar), which serves to slow the species that are ejected from the target with initial kinetic energy of a few 10’s of eV. The slowed atoms recombine in the gas phase to form nanoparticles, which are easily collected on an appropriately placed substrate. The experimental setup is presented in Figure 1(a), and a false color photograph of a TTFA plume is presented in Figure 1(b).

![Fig. 1. (a) Schematic of the TTFA experiment. (b) photograph (false color) showing light emission from the ablated material.](image)

For the work described here, the target consisted of a thin film (20 nm) of Ag that was sputter deposited onto a 5 cm diameter disk of UV-transparent fused silica. This structure was irradiated from the back side through the silica support with the output of a KrF excimer laser ($\lambda=248$ nm). The laser beam struck the target at an angle of 45°, and the laser energy density at the target was 0.6 J/cm². The target was rotated after each laser pulse in order to expose a fresh area for subsequent ablation.

Ablation was carried out in vacuum ($p=2\times10^4$ Pa) and with the ablation chamber filled with Ar at pressures of 133, 266, and 665 Pa. Ag nanoparticles were deposited onto TEM grids placed 5 cm from the target on a substrate of single crystal Si. Each deposition was carried out by using a single laser pulse, and the substrates were nominally at room temperature.
during deposition. All nanoparticle samples described here were prepared by ablating different area of the same target.

3. Results and Discussion

Shown in Figures 2(a)-2(d) are TEM micrographs of Ag nanoparticles deposited by TTFA; each sample was prepared by using a single laser pulse.

![Fig. 2. TEM micrographs of Ag nanoparticles synthesized by TTFA in: (a) Vacuum, (b) 133 Pa, (c) 266 Pa, and (d) 665 Pa of Ar.](image)

All micrographs were acquired with the same magnification, and the scale bar seen in Figure 2(a) represents a distance of 20 nm. The micrograph presented in Figure 2(a) was obtained from a sample formed by TTFA in vacuum. There is no discernible agglomeration of the nanoparticles, and the largest particles have diameters less than 20 nm. Presented in
Figure 2(b) is a micrograph of the Ag nanoparticles formed by TTFA in 133 Pa of Ar. There appear to be additional, even smaller particles formed in 133 Pa of Ar. Presented in figure 2(c) is a micrograph acquired from a sample prepared in 266 Pa of Ar. It is interesting to note that there are numerous smaller nanoparticles as well as fewer of the larger particles. Presented in Figure 2(d) is a micrograph of the sample synthesized in 665 Pa of Ar. There is no evidence of agglomeration in any of the TEM micrographs shown in Figure 2. This is in contrast to previous work (Murray et al., 2006; Koehler et al., 2006) that reported extensive agglomeration of nanoparticles made by conventional pulsed laser ablation. The absence of agglomeration in the TTFA process is attributed to the smaller amount of material ablated per laser shot compared to the conventional process. There are no particles larger than 20 nm seen in Figure 2 or in other, lower magnification images.

![Histograms of Ag nanoparticle size distributions](image)

Fig. 3. Size distributions of Ag nanoparticles synthesized by TTFA in: (a) vacuum, (b) 133 Pa, (c) 266 Pa, and (d) 665 Pa of Ar.
Presented in Figures 3(a) through 3(d) are the Ag nanoparticle size distributions that were extracted from the TEM images. The distribution presented in Figure 3(a) was obtained from the sample made by TTFA in vacuum, and the inset shows an expanded region of the same distribution. The distribution of particles formed in vacuum is bimodal, with one component centered near 2 nm and another near 8 nm. We hypothesize that the 8 nm component was formed by splashing of a very thin, transient liquid layer on the irradiated target. Gated, high speed images recorded during ablation indicated the presence of a slow (~ 100m/s) component that is attributed to hot, Ag nanoparticles ejected directly from the target. The 2 nm component is most likely due to gas phase recombination of ablated atomic and molecular species. Indeed, analysis by optical emission spectroscopy showed a large (excited) atomic Ag component in the ablated flux. Furthermore, gated, high speed images recorded during ablation (in vacuum) indicated the presence of a fast (~ 3 km/s) component due to fast atomic Ag (which was confirmed by optical emission spectroscopy). The observation of a fast atomic component suggests that TTFA deposition in vacuum is a process in which a thin film of Ag is formed on the substrate by the atomic component, and the slower nanoparticles land on this nascent thin film some time later.

Shown in Figure 3(b) is the size distribution of Ag nanoparticles formed by TTFA in 133 Pa of Ar. Comparison of Figures 3(a) and 3(b) indicates that the number of small (~ 2 nm) Ag nanoparticles formed by TTFA in Ar is nearly an order of magnitude greater than that formed in vacuum. This is reasonable given the fact that these species were formed by recombination of ablated Ag atoms following collision with background Ar. The inset in Figure 3(b) presents an expanded portion of the size distribution. It can be seen that the most probable nanoparticle size is approximately 2 nm. It can also be seen that the larger (8 nm) component is still present, albeit with a smaller intensity.

Presented in Figure 3(c) is the size distribution of nanoparticles formed in 266 Pa of Ar. The smaller component is nearly a factor of 3 more intense than seen at 166 Pa, and the most probable size is near 1 nm. It is interesting to note that the most probable size of the larger component is near 4 nm, suggesting that the hot, molten nanoparticles splashed from the target undergo enough collisions with background Ar (and with slowed atomic Ag and with nanoparticles newly formed by gas phase recombination) to undergo fragmentation by the time they land on the substrate.

The size distribution of particles formed in 665 Pa of Ar is shown in Figure 3(d). The overall number of particles (large and small component) is smaller than that seen at lower pressure; this suggests that, at this pressure, there are a sufficient number of collisions with background gas (and other species) that prevent the nanoparticles from reaching the substrate. These data illustrate the importance of finding the proper combination of background pressure and substrate distance to collect the optimal number of nanoparticles.

TTFA of Ag in Ar under the current conditions results in the formation of non-agglomerated nanoparticles with a most probable size of between 1 and 2 nm. The most probable size can, most likely, be altered by varying the nature of the background gas (i.e. by using He instead of Ar), the background gas pressure, and the target-substrate distance. The results presented here were obtained with a laser energy density at the target of 0.6 J/cm².
Ablation at energy densities greater than \( \sim 1 \text{ J/cm}^2 \) resulted in damage to the fused silica support structure (as indicated by the presence of excited Si lines in the optical emission spectra). Ablation at energy densities less than \( 1 \text{ J/cm}^2 \) caused no detectable damage to the silica support and no detectable contamination of the nanoparticle deposit.

The TTFA process allows one to synthesize nanoparticles with minimal contribution from larger particles. This is in contrast to the conventional laser ablation process in which larger, splashed particles are formed in addition to nanoparticles. We hypothesize that this difference lies in the two distinct target geometries. Conventional laser ablation entails irradiating a bulk target from the front. With this configuration, the region of highest transient temperature rise lies at the surface of the target; the temperature rise will decrease as a function of depth into the target. At some critical distance from the surface, the temperature rise will be insufficient to cause explosive ejection of atomic species but will be sufficient to cause target melting. At this point and deeper, the transient liquid layer of molten target will be formed, and this will be the source of large particles that are splashed from the target. In contrast, TTFA entails irradiating the target film from the back side. In this geometry, the region of highest transient temperature rise will lie at the interface between the target support and target film. Target material at this interface will be predominantly atomized, and regions away from the interface (toward the target surface) will experience smaller temperature rises. At some critical distance from the interface, the temperature rise will be insufficient to cause explosive ejection but will be sufficient to melt the target. By choosing a target thickness that is less than this critical distance, one can ablate a target with minimal melting and therefore with a minimal amount of splashed particles.

4. Conclusion

Well dispersed Ag nanoparticles have been formed by TTFA. The nanoparticles were deposited on room temperature substrates, had a most probable size between 1 and 2 nm, and were not agglomerated. The nanoparticle deposit produced by TTFA showed no evidence of the larger particles \( \mu \text{m-sized} \) commonly observed from conventional pulsed laser ablation from a bulk target. Synthesis of nanoparticles by TTFA should be possible for any material that can be made as a thin film target and may enable the unique properties of isolated, non-agglomerated nanoparticles to be exploited more fully.

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6. References

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