NanoSpray^{SM} Combustion Processing Technology for Nanomaterials Fabrication

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ABSTRACT

NanoSpray^{SM} Combustion Processing technology is based on a proprietary atomization system known as a Nanomiser® device. Coatings with various microstructures are deposited through Combustion Chemical Vapor Deposition (CCVD) mode. The NanoSpray^{SM} CCVD process can be easily scaled-up for continuous production and can be easily integrated to existing production lines. It has produced many nanostructured thin films for various applications, including epitaxial dielectric thin films for high performance capacitors and tunable microwave devices, superhydrophobic coatings on various substrates, ceramic barrier coatings on polymers for food packaging, antimicrobial coatings, and nanocomposite thin films (ceramic matrix embedded with metal nanoparticles) for optical filter applications, to name a few. The NanoSpray^{SM} CCVD technology can process a wide range of substrates including ceramics, metals, glass, and plastics with complex shapes of virtually any size.

Keywords: nanostructure, superhydrophobic, durable, coating, CCVD

1 INTRODUCTION TO THE NANOSPRAY^{SM} CCVD TECHNOLOGY

*n*Gimat produces nanoEngineered Materials™ using its proprietary NanoSpray^{SM} Combustion Processing technology [1-3]. This innovation is based upon a proprietary atomization system, the Nanomiser® device, which produces sub-micron liquid aerosols that are used to make thin film coatings and nanopowders. With this technology, thin film coatings are deposited onto substrates in the open atmosphere by way of the CCVD process, as shown in Figure 1. In the NanoSpray^{SM} CCVD process, precursors, such as low-cost metal nitrates or 2-ethylhexanoates, are dissolved in a solvent, which typically also acts as the combustible fuel. By using bio-sourced solvents such as alcohols, the carbon foot print of NanoSpray^{SM} Combustion processing is very small since very little electricity is used. This solution is atomized to form submicron droplets, and these nano-droplets are then conveyed by an oxygen-containing stream to the flame where they combust in a manner similar to a premixed gas fuel. In CCVD of thin film coatings, the substrate is coated by simply drawing it over the flame plasma. The flame provides energy required for the precursors to react and to vapor deposit on the substrate. Substrate temperature is an independent process parameter that can be varied to actively control the deposited film's microstructure.

The conventional CVD process requires precursors with sufficiently high vapor pressures, frequently necessitating the use of expensive materials, and often produces toxic fumes that must be carefully treated, i.e., "scrubbed". Other vapor processes use significant amounts of electricity which is primarily sourced by fossils fuels. In contrast, the NanoSpray^{SM} Combustion Processing technology uses a wide range of inexpensive soluble precursors that do not need to have a high vapor pressure. Hence, precursors for the technology tend to be between 10 and 100 times less expensive than those used in traditional CVD processes.

The technology has significant promise to overcome many shortcomings of traditional vapor deposition techniques while yielding equal or better quality thin films and coatings at lower cost. The ability to deposit thin films in the open atmosphere enables continuous, production-line manufacturing. As a result, throughput potential is far greater than with conventional thin film technologies, most of which are generally restricted to batch processing. Thus, *n*Gimat's platform processing methods are vital to materials innovation and have an advantage in commercial production.

The key advantages of the CCVD technique include:

- Open-atmosphere processing
- Inexpensive precursors
- Outstanding microstructure and composition control
- High quality at low cost
- Wide choice of substrates, including ceramics, glass, metals, and plastics
- Continuous production capability
- No line-of-sight limit
- Precise control of coverage area
- Straightforward integration into existing production lines
- Environmentally friendly

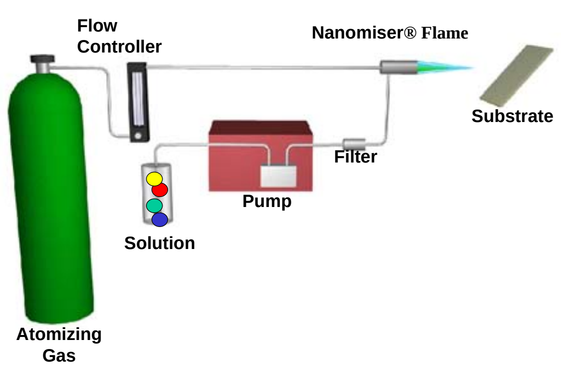

Figure 1. Schematic representation of the CCVD system

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2 NANOCOATINGS PROCESSED BY THE CCVD TECHNIQUE

2.1 Thin Films with Various Microstructures

By adjusting process parameters as well as solution concentrations and constituents, the NanoSpray^{SM} CCVD technology has produced many nanostructured thin films with different structures for various applications. Figure 2(a) shows an epitaxial BST dielectric thin film on sapphire for high performance capacitors and tunable microwave devices. In addition, nanostructured multilayer STO/BST thin films with up to 72 layers have also been successfully deposited onto sapphire substrate for high frequency high power microwave applications. Coplanar waveguide devices were fabricated on those multilayer dielectric thin films. A dielectric constant up to 915 and a tunability up to 42% at 40 V have been achieved. The lowest insertion loss of 1.82 dB at 40 GHz was obtained. For a thin film with a special dopant, a FOM of 4820 was achieved, compared to a FOM of 1537 on a standard single layer BST film (*n*Gimat control). Figure 2(b) shows a smooth and dense hard thin films and a columnar microstructure with high surface area for electrochemical applications. Multilayer corrosion resistant thin films, as shown in Figure 2(c), have also successfully deposited onto Al alloys. In addition, as shown in Figure 2(c), nanocomposite thin films with metal nanoparticles embedded in glass matrix have also been developed on glass and plastic substrates for optical filter applications. The absorption wavelength range can be easily adjusted by controlling the metal material, metal particle size, and metal composition.

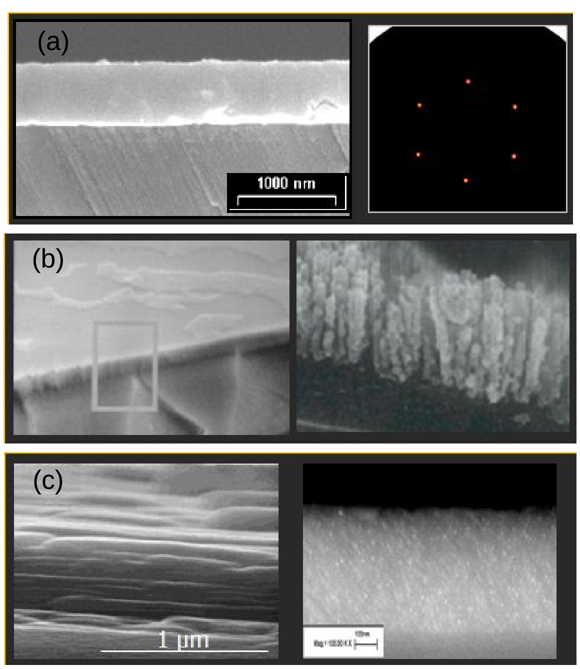

Figure 2. SEM images of thin films with different microstructures by the CCVD process

2.2 Superhydrophobic Coatings

Studies of superhydrophobic self-cleaning surfaces have been attracting increasing interest in recent years for both fundamental research and practical applications. The applications of superhydrophobic self-cleaning surfaces include architectural glass, automotive glass, solar panels, shower doors, and nanochips, etc. [1-3]. Wide usage of self-cleaning surfaces will result in huge energy savings by removing the need for washing, scrubbing, and chemical polishing of windows, ceramics, and other surfaces. In addition to a reduction in cleaning requirements, these superhydrophobic surfaces have additional benefits, such as improved safety when driving in severe rain and snow, and improved efficiency in solar cells.

By using the NanoSpray^{SM} CCVD technique, *n*Gimat has successfully developed nanostructured hyper-transparent superhydrophobic coatings on ceramics, glass, metals, plastics, and paper substrates. A water contact angle of 170^o and a rolling angle of less than 5^o have been achieved [3]. In addition, these coatings show superoleophobicity as well. A contact of 150^o has been obtained by using oleic acid. Due to the excellent performance, *n*Gimat has signed a license agreement with a major international automobile manufacturer to commercialize the technology for automobile windshield applications. By collaboration with the automobile company, a novel device, WRIN, was designed and manufactured. By the combination of the WRIN device and the CCVD process, robust superhydrophobic coatings have been developed on windshield glass, as shown in Figure 3. The coatings with is microstructure not only show superhydrophobicity, but also high durability. The test by the automobile manufacturer shows that after wiping the coating for 60,000 times by a standard automobile wiper the superhydrophobicity was kept, implying the superhydrophobic coatings are suitable for practical applications.

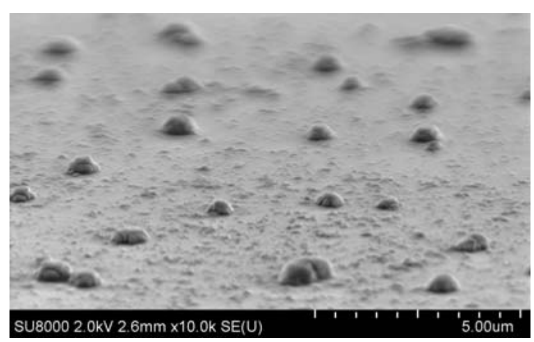

Figure 3. Contact angle of SiO_2 based coatings as a function of abrasion pass with different compositions

2.3 Antimicrobial Coatings

For centuries, silver has been known to have antimicrobial properties and has been used to treat a variety of diseases and infections. Contemporary research on silver as an antimicrobial agent tends to focus on nano-scale silver (nanosilver), owing to its improved antimicrobial properties and its potential ability to be the active component in thin antimicrobial surface coatings [7-8]. Nanosilver has been used in the treatment of burn wounds to decrease healing time, to coat plastic catheters to reduce biofilm formation, and *in vitro* to inhibit HIV-1 virus from binding to host cells. The mechanism of antimicrobial silver nanoparticles with gram-negative bacteria was found to be an attachment to the bacterial membrane surface and disruption of the bacteria by penetrating it and releasing silver ions.

By using the NanoSpray^{SM} CCVD process, *n*Gimat has developed novel Ag based nanocomposite antimicrobial coatings on various substrates, including petri dishes, paper boards, and metals. The CCVD-based antimicrobial coatings are expected to be lower cost than silver nanoparticle coatings since the film consists solely of active antimicrobial components, comparatively less material is needed to achieve results similar to nanosilver-based paints. In addition these nanocomposite antimicrobial coatings don't discolor when exposed to air and light.

Figure 4 shows SEM images of the silver based nanocomposite antimicrobial coatings on stainless steel filter strands and Al plates.

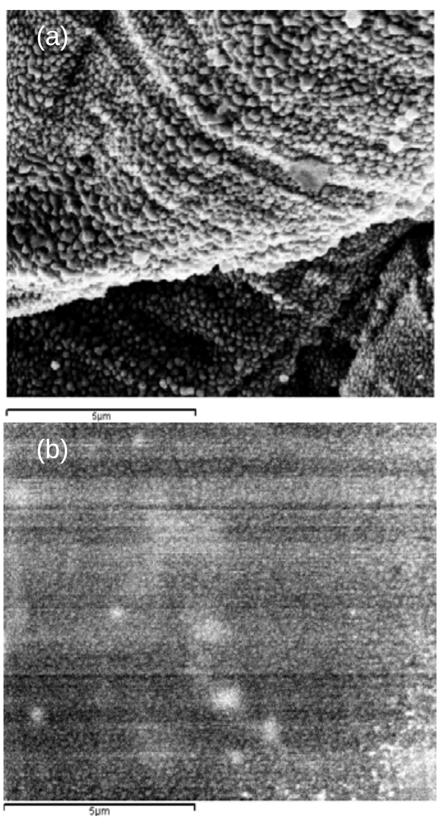

Figure 4. SEM images of antimicrobial nanocomposite coatings on (a) stainless steel filter strands and (b) Al plate

The antimicrobial performance of the selected nanocomposite coatings on three major bacteria is detailed in Table 1. All samples show a 99.999% reduction within one hour.

Inoculant	Sample	1 hour		2 hours	
		CFU/mL	% Reduction	CFU/mL	% Reduction
Salmonella	WI48A1	<10	99.999	<10	99.999
	Control 1	9400000	N/A	9300000	N/A
Listeria	WI48A2	<10	99.999	<10	99.999
	Control 2	11000000	N/A	14000000	N/A
E. coli	WI48B1	<10	99.999	<10	99.999
	Control 3	7600000	N/A	8500000	N/A

Table 1. Microbe reduction results selected antimicrobial nanocoatings

While actively develop novel nanostructured thin films and processes for different applications, *n*Gimat has commercialize several technologies by collaboration with industrial partners. Figure 5(a) shows a pilot roll-to-roll coater for depositing ceramic barrier coatings and interface improvement layers on polymer rolls for food packaging and enhancing adhesion and interface. By collaborating with a packaging company, *n*Gimat designed and manufactured pilot production equipment for producing anti-microbial coatings on paper boards or plastics for fresh produce packaging, as shown in Figure 5(b).

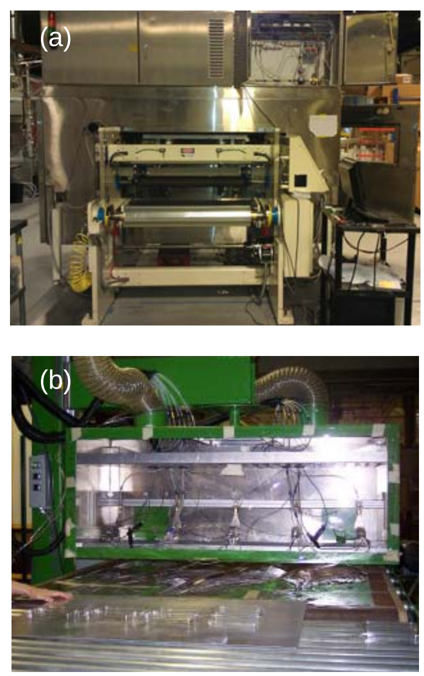

Figure 5. Continuous coater for fabricating antimicrobial coatings

3 SUMMARY

As a summary, *n*Gimat has successfully developed various nanomaterials and related processing technology for different applications based on its NanoSpray^{SM} CCVD technique. The NanoSpray^{SM} CCVD process offers many advantages that overcome many of the shortcomings of conventional CVD processing without sacrificing quality or performance. Due to its intrinsic simplicity and flexibility, the NanoSpray^{SM} CCVD technology enables accelerated development for new nanomaterials and applications.

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