ELECTROPLATING IN THE CONTEXT OF WORLDWIDE NANOTECHNOLOGY INITIATIVES

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Abstract

This paper deals with two important issues of interest to the electroplating and surface finishing industries. In the first part a summary is presented on recently established nanotechnology initiatives in various countries around the world. Program funding levels and core activities will be compared to provide a basis for assessing business opportunities for various industries. The second part of the paper looks at specific examples of nanostructures made by electrochemical methods currently at various stages in their development, or already in use. These include electrodeposition of monolithic pure metals and alloys, multi-phase composites, compositionally modulated multilayers, template manufacture by anodizing for nanodot and nanowire synthesis and electroplating of components for microelectromechanical systems.

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1) Worldwide Nanotechnology Activities

Nanotechnology is a relatively new multidisciplinary field in which many of the unusual physical and chemical effects observed only on the nanoscale (typically less than 100 nm) are utilized to create new materials, devices and objects with outstanding properties and functions never seen before. Nanotechnology includes several subdisciplines which can be summarized as shown in Fig. 1. The various subfields have their origin in different disciplines and were initially developed by scientists and engineers with different backgrounds. For example, nanostructured materials were originally developed by physicists and materials scientists, while bio-inspired nanotechnology was the domain of chemists and biologists.

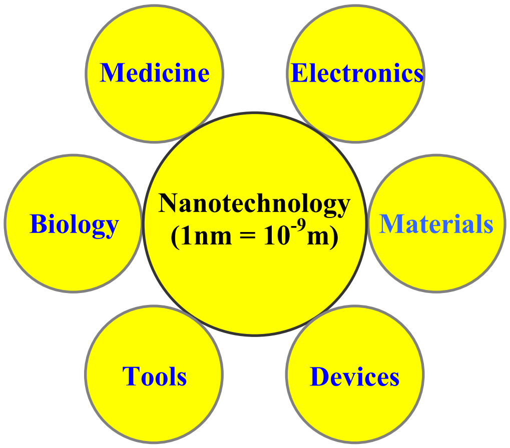

Figure 1: *Main focus areas of nanotechnology*

Today's' nanotechnology approach requires the breakdown of traditional barriers between these fields and strong collaborative efforts of people with quite different but complementary skill sets.

Table 1: Comprehensive Research Programs in Nanotechnology with Funding in Excess of US $ 100 Million/Year [Adopted from Ref. 1]

Country	Date Initiated
United States	January 2000
Japan	July 2001
South Korea	July 2001
European Community	March 2002
Germany	May 2002
Taiwan	September 2002

The enormous long term potential of nanotechnology in revolutionizing our approach to technology, which would ultimately result in increased productivity, a deeper understanding of nature and a better quality of live, was recognized in the late 1990's in many different countries. Table 1 [1] summarizes various comprehensive research programs in nanotechnology with government funding levels in excess of US $ 100 million per year, established after 2000.

President Clinton's initial nanotechnology initiative was launched in 2000 and was later enhanced under President Bush to become the 21st Century Nanotechnology Research and Development Act [e.g. 2]. Table 2 [1] shows a breakdown of funding levels for various Federal Departments or Agencies for 2000-2005 within the US National Nanotechnology Initiative (NNI). Over this period the total funding level increased by more than 360% to close to US$ 1 billion for 2005.

Table 2: Contributions of Key Agencies to NNI [Adopted from Ref. 1]

Federal department or Agency	FY 2000 Actual ($M)	FY 2001 Actual ($M)	FY 2002 Actual ($M)	FY 2003 Actual ($M)	FY 2004 Est. ($M)	FY 2005 Est. ($M)
National Science Foundation (NSF)	97	150	204	221	254	305
Department of Defense (DOD)	70	125	224	322	315	276
Department of Energy (DOE)	58	88	89	134	203	211
National Institutes of Health (NIH)	32	40	59	78	80	89
National Institute of Standards and Technology (NIST)	8	33	77	64	63	53
National Aeronautics and Space Administration (NASA)	5	22	35	36	37	35
Environmental Protection Agency (EPA)	-	6	6	5	5	5
Homeland Security (TSA)	-	-	2	1	1	1
Department of Agriculture (USDA)	-	1.5	0	0	1	5
Department of Justice (DOJ)	-	1.4	1	1	2	2
Total	270 (100%)	465 (172%)	697 (258%)	862 (319%)	961 (356%)	982 (364%)

Similar growth rates were observed in other countries such as Western Europe and Japan (Table 3, [1]). The total worldwide spending on nanotechnology reached US$ 3 billion by the year 2003.

Table 3: Estimated Nanotechnology R & D Expenditures During 1997-2003
(in U.S. $ millions/year) [Adopted from Ref. 1]

Region	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
West Europe	126	151	179	200	225	400	600
Japan	120	135	157	245	465	700	810
USA	116	190	255	270	422	600	774
Others	70	83	96	110	380	550	800
Total	432	559	687	825	1492	2347	2984
(% of 1997)	100	129	159	191	346	502	690

The funding comparison for Asia-Pacific countries presented in Table 4 [3] clearly shows that even smaller countries such as Australia, New Zealand or Singapore invest heavily in selected areas of nanotechnology R & D.

China, Taiwan and South Korea have established very aggressive programs with South Korea alone contributing US$ 1 billion over the five year period 2003-2007.

Table 4: Funding for Asia-Pacific countries in 2003
(For period 2003 – 2007) [Adopted from Ref. 3]

Country	**Population**	**Funding (5y)**	**Priority**	**Policy coordination**
Australia	19.2 million	100 M	BIO, IT	Common Core Facilities
China	1.2 billion	300 M+	MAT, ME	National and Regional Centers
Hong Kong	6.7 million	30 M	MAT, IT, EN	Centers of Excellence
India	1.0 billion	20 M+	MAT, MEMS	Centers of Excellence
Korea (South)	48.3 million	1 B	MAT, EL, BIO	National Centers and Core Facilities
Malaysia	21.8 million	23 M+	MAT	Centers of Excellence
New Zealand	4 million	50 M	MAT, EL	Centers of Excellence
Singapore	4.2 million	60 M	MAT, EL, BIO	Centers of Excellence
Taiwan	21.5 million	500 M	MAT, EL, MEMS	Common Core Facilities
Thailand	62 million	25 M	MAT, MEMS	National Centers

BIO = Biomedical, EN= Energy, EL=Electronics, IT=Information Technology, ME=Molecular Electronics, MAT=Nanomaterials, MEMS= Microelectromechanical Systems

The expected returns on investment in nanotechnology are huge. Table 5 [2] gives a breakdown by area of the projected market size by 2015, totaling US$ 1 trillion. The largest sectors are nanostructured materials and electronic components which probably reflects the relatively long nano research activity in these areas. For example, nanostructured materials were already introduced in the early 1980's [4] with considerable research efforts throughout the 1980's and 1990's. It was also during this period when most of the early fundamental work on nanostructured electrodeposits was carried out [5].

Table 5: Projected Nano Market Size by 2015 [Adopted from Ref. 2]

Materials	US$ 340 billion
Electronics	US$ 300 billion
Pharmaceuticals	US$ 180 billion
Chemicals	US$ 100 billion
Aerospace	US$ 70 billion
Sustainability	US$ 45 billion
Healthcare	US$ 30 billion
Nanotech Tools	US$ 20 billion

In view of the great potential for new business opportunities arising for the electroplating industries from the worldwide activities in nanotechnology, in particular nanostructured materials, AESF established the Nanomaterials Subcommittee in 2002. A first comprehensive paper on "Nanotechnology Opportunities for Electroplating Industries" was published by Plating and Surface Finishing in 2003 [6] and full day sessions on Nanomaterials were held at the 2003 SUR/FIN in Milwaukee and 2004 SUR/FIN in Chicago. It was also in 2004 that the Nanomaterials Subcommittee was accorded full Committee Status.

The remainder of this paper deals with specific examples looking at current and future application areas for electroplating and surface finishing industries in nanotechnology.

2) Monolithic Metal Nanostructures

Synthesis methods for the production of monolithic electrodeposits with crystal sizes less then 100 nm have been developed since the early 1980's. One of the earliest systems that was extensively studied was Ni-P [7, 8], using bath formulations very similar to the ones developed by Brenner et al. [9], and direct current plating. Particular emphasis was on electrodeposits with very narrow grain size distributions and average grain sizes in the 5-50 nm range. An example of such a structure is shown in Figure 2. In the late 1980's emphasis shifted towards more complex alloy systems (e.g. Ni-Fe, Co-Fe, Ni-Mo, Zn-Ni, Ni-Fe-Cr, etc.) and the application of pulsed current deposition of pure metals such as Ni, Co or Cu [10, 11].

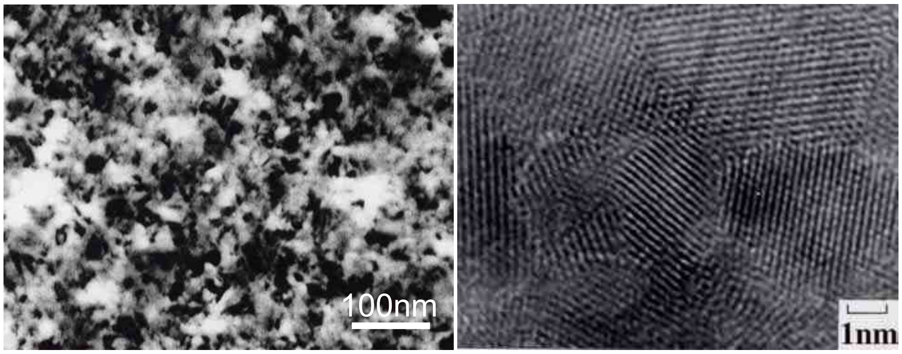

Figure 2: *Bright field (left) and high resolution (right) electron micrographs of nanocrystalline Ni with equiaxed grain shape and narrow grain size distribution*

During electrodeposition, two competing factors control the grain size of the electrodeposit. When a metallic ion in solution is reduced on a substrate it can either contribute to the nucleation of a new crystal or the growth of an existing crystal. Nanocrystal formation requires a set of operating parameters (e.g. bath composition, pH, temperature, current density, current on and off times during pulse plating, agitation, etc.) which promote massive nucleation throughout the entire electrodeposition process. What must be avoided are conditions that would result in a transition with increasing deposit thickness from initially fine grained structure to coarse columnar structure often observed in conventional electrodeposits [e.g. 12].

Electrodeposition processes have been developed for the synthesis of nanocrystalline deposits in many different shapes and forms [5, 6]. These range from thin and thick corrosion and wear resistant coatings to electroformed sheet and plate products for structural, magnetic or electronic applications. This technology can be easily incorporated with little extra costs in conventional electroplating facilities using a variety of different plating approached including rack plating, reel-to-reel plating, barrel plating, brush plating or continuous strip/foil plating.

As a result of their small grain size monolithic electrodeposits show significant improvements in many properties compared to their conventional counterparts. These include considerable increases in hardness, tensile strength, wear resistance and corrosion resistance all of which are well understood in terms of the underlying physical and chemical principles of nanomaterials [13]. The earliest applications of this type of nanocrystalline deposits was the in-situ electrosleeve nuclear reactor steam generator tubing repair technology developed in Canada since the early 1990's for both Canadian and US nuclear reactors [14]. In this process, steam generator tubes (e.g. Alloys 600 or 400) whose structural integrity was compromised by localized degradation phenomena (e.g. by intergranular corrosion or pitting) were repaired by electroplating their insides with a 1 mm thick nanocrystalline Ni-P alloy to restore a complete pressure boundary. In order to give the required combination of strength, ductility, corrosion resistance and long term stability at temperatures in the 280-350^{0}C range, the grain size of the electrosleeve was adjusted in the 50-100 nm range. It should be noted that, in 1994, this electrodeposited nanostructure was the first large scale industrial application of any structural nanomaterial in the world. It saved the Ontario utilities alone several hundred million dollars.

3) Structurally Graded Nanometals

Monolithic nanometals with narrow grain size distributions exhibit remarkable mechanical properties in terms of hardness, tensile strength and wear resistance. However, their ductility is usually compromised, regardless of the processing route [15]. This is mainly the result of restricted dislocation activity at such small grain sizes. In recent years it has been recognized that considerable ductility can be restored in the materials through broader or bi-modal grain size distributions [15]. In view of this we have developed electroplating conditions for a variety of structurally graded nanomaterials [Fig. 3]. These include bi-modal distributions [Fig. 3a], alternate layers of large and small grain sizes [Fig. 3b] and grain size gradient deposits [Fig. 3c]. In such structures the small gain size regions provide the outstanding strength while the larger grains allow for sufficient dislocation activity to result in reasonable ductility values.

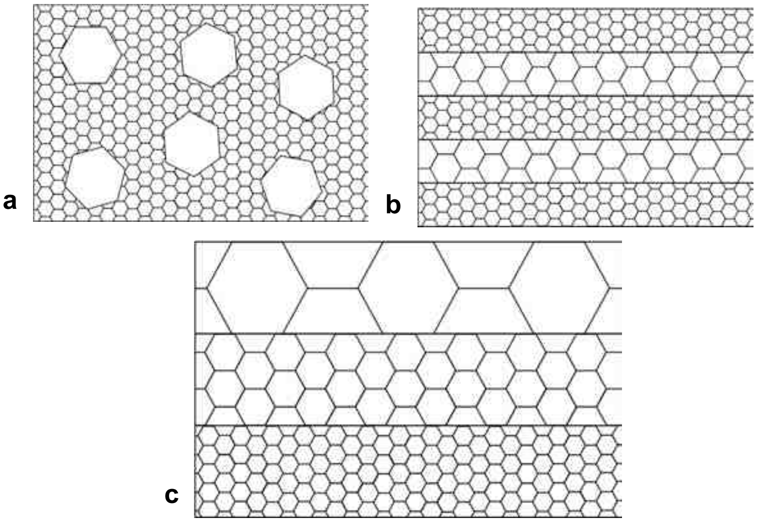

Figure 3: *Schematic diagrams showing various types of structurally graded nano-materials: a) bimodal grain size distribution; b) alternate layers with different grain sizes and c) grain size gradient structure.*

4) Nanocomposites

Composite coatings consisting of conventional polycrystalline metal electrodeposits with second phase particles co-deposited during electroplating have been in use for many years for applications such as increased wear resistance or reduced surface friction coatings [12]. Over the past several years this concept has been extended to nanocrystalline materials [6, 13, 16]. Figure 4 shows several examples of submicrocrystalline / nanocrystalline second phase particles or fibres embedded in a nanocrystalline metal matrix. Examples of second phase particles/fibres include Al_2O_3, TiO_2, SiC or B_4C for improved wear resistance applications, carbon nanotubes for increased strength or Teflon and MoS_2 for low friction coating applications. An alternative route to particle co-deposition is to first produce an alloy deposit as a supersaturated solid solution. Subsequent heat treating of such heat-treatable coatings produce the second phase particles by a precipitation reaction [5].

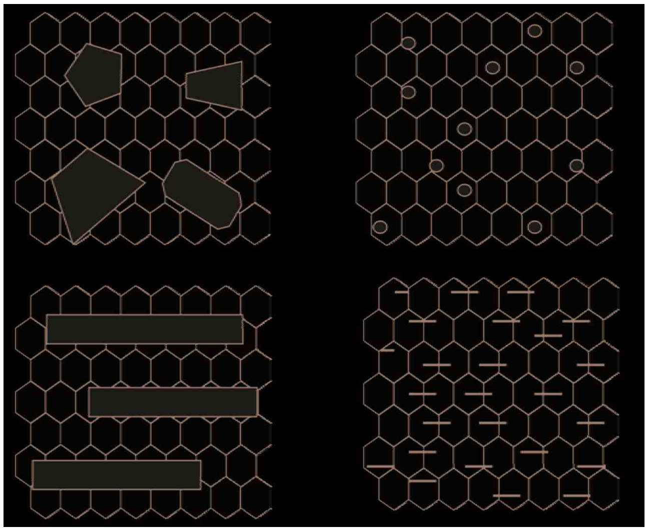

Figure 4: *Examples of nano-composite electrodeposits.*

5) Compositionally Modulated Alloy (CMA) Nanostructures

Compositionally modulated nanostructures consist of alternating layers of deposits with different chemical composition as schematically shown for Ni-Cu multilayers in Fig. 5. The critical nano-dimension in this case is the thickness of the individual layers. Because of their unusual microstructure these materials exhibit unexpected properties such as increased strength, elastic constants and tribological properties, as well as outstanding electromagnetic properties. In fact, one of the most advanced applications of CMA's are alternating layers of ferromagnetic and non-magnetic layers to produce the giant magnetoresistance effect which has already resulted in widespread industrial applications in the recording head industry [17]. CMA's can be produced by many different methods including physical vapor deposition, chemical vapor deposition and electrodeposition. Electrodeposition approaches include rotating substrate methods and potential-stepping methods. In the rotating substrate method two physically separated baths are used and the cathode is rotated between the two baths. In the potential stepping methods, ions of the two metallic species are contained in the same plating bath. By periodically stepping the potential between predetermined values, the relative deposition rates of the two species creates the required concentration changes in the multilayers. Using these approaches, many CMA structures have been produced by electrodeposition such as Ag-Pd, Cu-Ni, Cu-Pb and Ni-P with moduclation wavelengths down to few nm [18, 21]. Even nanomodulated ceramic structures have been produced by this technique [22].

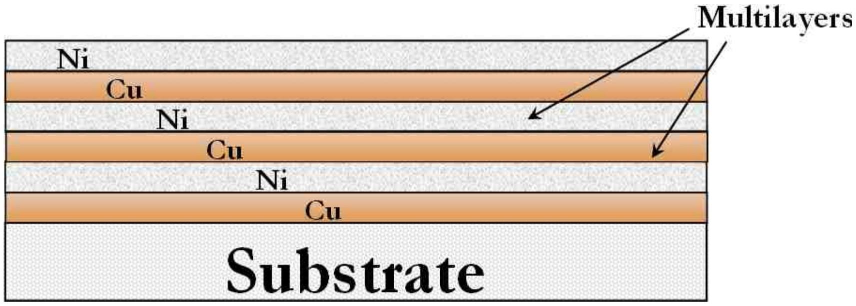

Figure 5: *Schematic diagram showing a compositionally modulated alloy deposit.*

6) Template Nanotechnology by Anodizing

Anodizing of aluminum is a widely used finishing process to improve the surface characteristics of aluminum parts [23-25]. This process involves the artificial build up of the natural protective aluminum oxide layer from a few nanometers thickness to tens or even hundreds of micrometers by making the aluminum part the anode in a suitable electrolyte. Under anodizing conditions a porous oxide layer with regular or irregular arrangements of hexagonal columns with pores extending from the free surface down to the initial barrier layer is produced (see top and side views in Fig. 6a, b). For requirements such as scratch or corrosion resistance the porous aluminum oxide is sealed, for example by boiling in water which hydrates and expands the oxide to effectively close the pores. In color anodizing (for example for architectural applications) the pores are impregnated with dyeing compounds or mineral pigments of different color, prior to sealing (Fig. 6c).

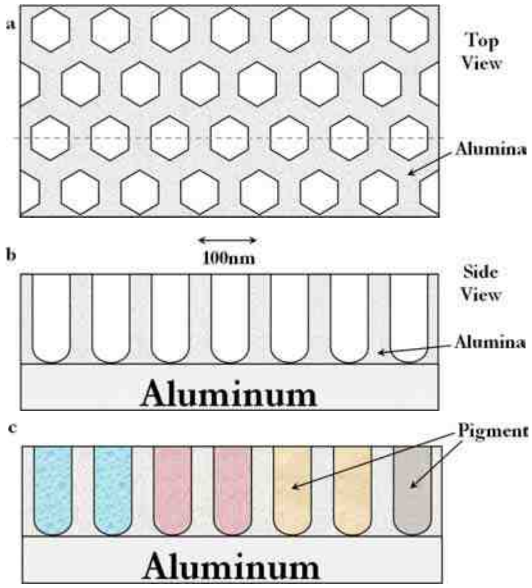

Figure 6: *Nanoporous aluminum oxide produced by anodizing:*
a) *top view showing hexagonal pore structure;* ***b)*** *cross-sectional view and* ***c)*** *coloring by pigment addition.*

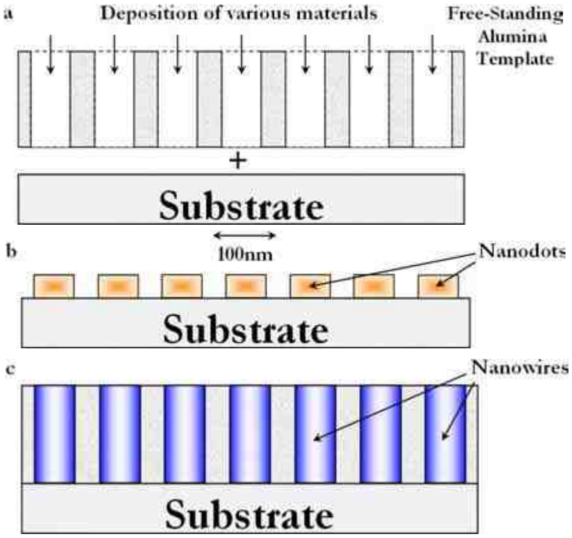

Figure 7: *Application of nanoporous alumina template in nanodot and nanowire synthesis*

Over the past 10 years the basic anodizing approach has been further developed to produce highly ordered nanoporous honeycomb oxide structures for use in nanostructure synthesis by the template approach [26]. In this process the porous alumina film is extracted by dissolution of the aluminum substrate and used as a free-standing mask to produce, by vapor deposition, structures such as nanodots or nanowires of various materials, in particular semiconductors (Fig. 7). For example regular arrays of so-called quantum dots produced by this method have very interesting electrical properties resulting from electron state confinement in crystals with very small external sizes.

7) Microsystem Technology

Microsystems can be described as intelligent miniaturized systems that combine sensing and/or actuating functions with processing functions. Such systems are typically multifunctional, combining two or more electrical, mechanical, optical, chemical, biological or magnetic properties such as in Microelectromechanical Systems (MEMS). Many microsystems are produced by various micromachining methods on a single substrate in form of a monolithic system (for example an all Si device). However, other designs require metallic components which, in most cases, are produced by electrodeposition methods (e.g. the so called LIGA process) [e.g. 27]. Figure 7 shows a series of schematic diagrams of the various process steps involved in making a microgear by the LIGA process. The first steps are preparation of mask and mold into which the metal is to be deposited. Traditional LIGA parts have a columnar grain structure with very high grain shape anisotropy. As the size of the microsystem parts are getting smaller and smaller this structure becomes unacceptable because it leads to loss in overall strength, non-uniform properties and unreliable system performance [28]. We have recently shown that these problems can be alleviated by adopting nanostructured electrodeposits for microsystem components [29, 30]. By using equiaxed nanocrystalline Ni, Co or Ni-Fe deposits, property variations due to grain size/shape anisotropies have been eliminated and the overall performance of the components in terms of specific strength, elastic energy storage capability, thermal shock resistance and reduced eddy current losses were improved enormously.

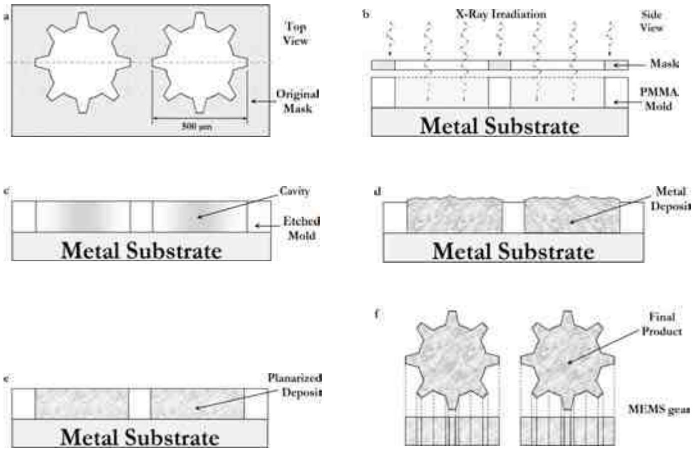

Figure 8: *Various steps in the production of a MEMS gear by electrodeposition*

8) Summary

Nanotechnology is one of the fastest growing areas in science, engineering, biology and medicine and is expected to have a tremendous impact on society over the next few decades. In view of the expected returns on investment many countries have established their own nanotechnology platforms with substantial government funding. Many industries have already formulated their plans for strategic positioning in this very broad field. Electroplating and surface finishing industries have a lot to offer in this area in particular when it comes to meeting the challenges in providing new nanostructured materials of improved performance or manufacturing capabilities to produce structures, devices and systems on a micro/nanoscale.

9) Acknowledgments

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