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**SYNTHESIS, PROPERTIES, AND APPLICATIONS
OF NANOPHASE MATERIALS***

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Work on the synthesis, properties, and applications of nanophase materials has developed rapidly during the past decade. A wide variety of methods now exist for their production, including several plasma-based processes. The possibilities for engineering new materials with unique or improved properties for a number of applications is now evident from the extant research results. A brief review is presented here along with some examples of useful application areas and some thoughts for the future of this field.

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Work on the synthesis, properties, and applications of nanophase materials has developed rapidly during the past decade. A wide variety of methods now exist for their production, including several plasma-based processes. The possibilities for engineering new materials with unique or improved properties for a number of applications is now evident from the extant research results. A brief review is presented here along with some examples of useful application areas and some thoughts for the future of this field.

Introduction

Nanophase materials have now been investigated for more than a decade using a rather wide range of experimental methods [1-3]. The structures and properties of these new materials, which are artificially synthesized from nanometer-sized clusters or powders, have been elucidated in a number of important areas and the relationships among these areas are beginning to be understood. Various investigations of their chemical, mechanical, electrical, magnetic, and optical behavior have demonstrated the possibilities to engineer the properties of nanophase materials through control of the sizes of their constituent clusters or powders and the manner in which these constituents are assembled [4-6]. There are, however, tremendous opportunities remaining for creative new tailored synthesis and processing methods. Some aspects of our present understanding of nanophase materials and their properties are briefly presented here, along with some thoughts regarding a few critical future research needs in the field of nanophase materials and their applications.

Interest in the physics of condensed matter at size scales larger than that of atoms and smaller than that of bulk solids has grown rapidly because of the increasing realization that the properties of these mesoscopic atomic ensembles are different than those of conventional solids. Thus, interest in artificially assembling materials from nanometer sized building blocks arose from discoveries that, by controlling their sizes in the range of 1-100 nm and the assembly of such constituents, one could begin to alter and prescribe the properties of the assembled nanostructures. Nature had apparently already learned well the value of nanostructuring, since many examples of naturally created nanostructures, formed chemically under ambient conditions, can be found in biological systems from sea shells to the human body.

Nanophase materials represent only one class of the broader area of nanostructured materials modulated over nanometer length scales. Nanostructured materials can be assembled with modulation dimensionalities of zero (atom clusters or filaments), one (multilayers), two (ultrafine-grained overlayers or coatings or buried layers), and three (nanophase materials), or with intermediate dimensionalities [5]. Thus, nanocomposite materials containing multiple phases can range from the most conventional case in which a nanoscale phase is embedded in a phase of conventional sizes to the case in which all the constituent phases are of nanoscale dimensions. All nanostructured materials share three fundamental features, which make them useful to consider as a set: atomic domains (grains, layers or phases) spatially confined to less than 100 nm in at least one dimension, significant atom fractions associated with interfacial environments, and interactions between their constituent domains.

Synthesis and properties

A large number of methods exist for the synthesis of nanophase materials [4,7]. They include synthesis from atomic or molecular precursors (chemical or physical vapor deposition; gas-condensation; chemical precipitation; aerosol reactions; biological templating), from processing of bulk precursors (mechanical attrition; crystallization from the amorphous state; phase separation), and from nature. It is generally preferable to synthesize nanostructured materials from atomic or molecular precursors, in order to gain the greatest control over a variety of microscopic aspects of the condensed ensemble, but other methodologies can often yield very useful results. Several plasma-based methods have already been usefully applied to the synthesis of nanophase materials [8-14]. However, the surface chemistries of the plasma-produced powders need to be critically investigated for residual contamination from precursors, which can inhibit their subsequent utilization. Yet, novel high-temperature chemical synthesis and processing methods for creating tailored nanostructures are sorely needed, especially ones that can carefully control surface and interface chemistry.

In the creation of nanophase materials, the ability to control the size and size distribution of the constituent phases or structures is of primary importance. While this is of course a necessary requirement of nanostructuring, it is generally not a sufficient condition for their application, as will be discussed below; surface chemistry can also play a decisive role. The desirable cluster or powder sizes are generally below 100 nm, since it is in this size range (and frequently below 10 nm) that various properties begin to change significantly owing to confinement effects. Spatial confinement can in general affect any property when the size of the atomic ensemble becomes comparable to or smaller than a critical length scale for the mechanism that is responsible for that property. Examples can be as diverse as the "blue" (high-frequency, short-wavelength) shifts of the optical absorption in semiconducting clusters when their sizes fall below the Bohr radii (ca. 5-50 nm) of the excitonic (electron-hole pair) states responsible for absorption and the increased strengthening of normally soft metals when their grain sizes fall below the critical length scales (ca. < 50 nm) for the sources of dislocations (the defect responsible for easy deformation) to easily operate at conventional applied stresses.

The chemical compositions of the constituent phases in a nanostructured material are also of fundamental importance, as they are to the performance of conventional materials. This not only relates to average compositions, but also invariably to chemical gradients within the constituent phases or structures and especially those near surfaces and interfaces. Indeed, the chemistry of the surfaces of the constituents, as well as that of the subsequently formed interfaces on assembly, can often play a crucial role in the ability to use these materials. This can be a real problem in the synthesis of nanophase powders from gaseous or liquid precursors, where residues in the form of surface contaminants (even at submonolayer levels) can prevent the subsequent use of these powders in consolidated or high-surface-area forms. Another aspect of nanostructured materials that one would like to be able to control in their synthesis is the nature of the interfaces created between constituent phases and, hence, the nature of the interactions across the interfaces. Both the local structure and chemistry of the interfaces are important in this regard.

The properties of nanophase materials are determined by the interplay among these three features (domain size, composition, and interfaces). In some cases, one or more of these features may dominate the particular property in question. Thus, one wants to be able to synthesize nanophase materials under well-controlled conditions, but with an eye toward the particular property or properties of interest in subsequent applications. The degree of control available, of course, depends upon the particular synthesis method being used to create the given material. In some cases, a rather simple nanophase synthesis and processing route can yield the desired property. In other cases, a considerably greater degree of sophistication will be required to effect the required property or properties. An example of the former case could be the relatively simple need for a stronger copper conductor. Examples of the latter case may be the need to nanostructure a functionally-gradient material or a multifunctional, smart material with a variety of constituents and structural scales.

Applications

Among the various artificially synthesized nanostructures, multilayered materials have had the longest history, one that has already seen applications in semiconductor devices, strained-layer superlattices, and magnetic multilayers. The technological potential of multilayered quantum hetero-structure semiconductor devices was recognized as early as the 1970s in the rapidly expanding electronics and computer industries and helped to drive advances in this exciting new field. Since the 1980s there has been a rapid expansion of research on isolated atom clusters and an increased understanding of their potential as the constituents of new materials [1]. During the past several years, exciting progress has been made in the physics, chemistry, biology, and materials research communities in characterizing and understanding these materials. A few examples are given here.

The chemical reactivity of nanophase materials, with their potentially high surface areas compared to conventional materials, can also be significantly enhanced, a property long utilized in the catalysis community. Since clusters or ultrafine powders can be assembled by means of a variety of methods, there can be an excellent degree of control over the total available surface area in the resulting self-supported nanophase ensembles. Thus, one can maximize porosity for obtaining very high surface areas, remove most of it via consolidation, but retain some to facilitate low-temperature doping or other processing, or fully densify the nanophase material. Also, control of chemical composition can be readily achieved, since rapid atomic diffusion paths are plentiful and diffusion distances are short in the clusters. Measurements of the decomposition of hydrogen sulfide over lightly consolidated, high-surface-area nanophase titanium dioxide with a rutile crystal structure have clearly demonstrated the potential for enhanced chemical reactivity of nanophase materials [15]. Nanophase rutile is far more reactive initially than other available forms of titanium dioxide and, more importantly, remains so even after extended exposure to the hydrogen sulfide at 500°C. This enhanced activity results from a combination of unique and controllable features of the nanophase material, its high surface area combined with its rutile structure and its oxygen deficient composition. Such behavior should have significant future impact in a variety of catalytic and sensor applications, but great care must be exercised in the synthesis and processing routes to ensure proper control of surface chemistry and atomic defect populations.

Clusters of metals, intermetallic compounds, and ceramics have been consolidated to form ultrafine-grained polycrystals that have mechanical properties remarkably different and improved relative to their conventional coarse-grained counterparts [16]. For example, nanophase Cu and Pd assembled from clusters with diameters in the range 5 to 7 nm can have hardness and yield-strength values up to 500% greater than in the conventionally produced metal. This greatly increased strength arises from the increased difficulty in the spatially confined grains of nanophase metals in creating and moving dislocations, the defect normally responsible for the relatively easy deformation process in metals. In ceramics, on the other hand, which are normally difficult to deform and hence very brittle, cluster assembly yields a different benefit. Ceramics and conventionally brittle intermetallics can be rendered ductile (capable of easier deformation) by being synthesized from clusters with sizes below about 15 nm. This ductility results from the increased ease with which the ultrafine grains created by the clusters can slide by one another in a process called grain-boundary sliding, owing to the short diffusion distances required for the necessary local healing of incipient cracks that could otherwise form during this grain-over-grain sliding process. Such enhanced ductility should allow these materials in their nanophase state to be formed to near-net shapes by means of deformation processing methods previously applicable only to producing ductile metal parts. Nanocomposites consisting of metallic phases, ceramic and metallic phases (cermets), and ceramic phases in a variety of modulation dimensionalities also have considerably enhanced mechanical properties including increased strength and fracture toughness. It is very early in the development of these new materials, but the increased ductility exhibited by nanophase ceramics and intermetallics and the increased strength observed in nanophase metals and nanocomposites should find use in a variety of future technological applications, including those for which wear or corrosion resistance are important design criteria.

The ability to engineer the electrical properties of nanophase materials can also have a significant future impact. It has recently been demonstrated that even pure nanophase ZnO can exhibit varistor behavior with a small, but useable threshold voltage of 0.1 kV/cm of material for a 60 nm diameter grain size [17]. This compares with a value of about 4 kV/cm for a conventional, heavily-doped ZnO varistor material, where it is well known that the highly nonlinear I-V characteristics responsible for the varistor response (i.e., a constant voltage over a wide range of current) stem from grain-boundary conductivity effects. It is now further apparent from recent work on similarly-doped nanophase ZnO(B,Bi,Co,Cu,Sb,Sn) with 3-10 nm grain sizes that one can extend the varistor-active range up to 30 kV/cm [18]. It should thus be possible through nanostructuring to produce ZnO varistors with threshold voltages between at least 0.1 and 30 kV/cm by controlling the grain size and, hence, the number of grain boundaries loaded into the material and the amount and type of dopants loaded into the grain boundaries.

In magnetic multilayers, such as those formed by alternating layers of ferromagnetic Fe and Cr, the material can be nanostructured so that its electrical resistance is significantly decreased (by up to a factor of 2 depending upon the Cr layer thickness) by the application of a magnetic field of 2 T [19]. Such an effect, called giant magnetoresistance (GMR), occurs when the magnetic moments of the neighboring alternating layers (Fe) are arranged in an antiparallel fashion, so that application of the magnetic field overcomes the antiferromagnetic coupling and aligns the layers into a condition of parallel ferromagnetic ordering, strongly reducing the electron scattering in the system. Magnetoresistive materials are already being used in the magnetic recording industry as read heads, owing to their lower noise and improved signal handling capabilities. It is expected that nanostructured materials will have a significant future impact in this area as new materials are developed with stable GMR at room temperature that can operate at magnetic fields as low as about one mT. Discoveries that nanostructured materials other than multilayers (such as nanocomposites of magnetic Co clusters embedded in a nonmagnetic matrix of Cu or Ag [20,21] or magnetic plate-like NiFe deposits embedded in Ag [22]) also exhibit GMR should hasten the advent of their useful application. It seems that the modulation dimensionality and the material architecture play important roles in the resulting magnetic behavior and that a variety of nanophase materials will impact this area in the future.

The optical properties of assemblages of small semiconductor clusters have been found exciting from both the scientific and technological points of view. The optical absorption of CdS clusters with diameters in the nanometer size regime made by any of a variety of methods, including chemical precipitation in solutions or in zeolite supports, is rather different from that for bulk CdS. The optical absorption edge in isolated, noninteracting clusters is blue shifted to appreciably shorter wavelengths, owing to the effects of quantum confinement in these nanoscale clusters. However, when these clusters are synthesized in zeolite supports with increasing loading, such that they become close enough to begin to interact through quantum tunneling, the absorption edge begins to shift back toward bulk behavior [23]. A similar effect can be created by changing the sizes of the clusters in colloidal suspensions and thereby changing the degree of quantum confinement [24]. Hence, control of the average distance between clusters in the zeolite cages, even though they are not actually in contact, or control of the cluster sizes in a suspension can enable control over a macroscopic property of the assembled cluster ensemble. Thus, not only do such quantum size effects in clusters provide a basis for verifying our understanding of the electronic structure of condensed matter, they may also provide for engineered optical properties that will find useful future applications in optical and computing devices.

Another example of enhanced optical behavior in the nanoscale regime, which has gained much attention recently because of its potential for technological application, is porous Si formed by chemical etching that creates a bicontinuous array of nanometer-sized pores and Si "wires" [25]. The remaining nanostructured Si has an increased band gap caused by quantum confinement and an enhanced photoluminescence. Nevertheless, important questions regarding this latter property remain to be answered related to the surface chemistry of this material. It is possible that synthesis of porous Si by alternate methods could help to answer such questions and hasten the useful application of this material.

Future needs

There are tremendous opportunities for synthesizing nanostructured materials with new architectures at nanometer length scales from atomic or molecular precursors via the assembly of atom layers and clusters and by a myriad of other techniques now becoming available, such as nanoscale lithography and biological templating. Important keys to the future of nanophase materials will be (i) our ability to continue to significantly improve the properties of materials by artificially structuring them on these nanometer length scales and (ii) developing the methods for producing these materials in commercially viable quantities. There are, thus, very significant opportunities for developing creative new plasma-based synthesis and processing routes for the tailored nanostructuring of materials with new engineered properties. In developing these new methods, it is however imperative that an understanding of the important role of surface and interface chemistry in the assembly and resulting properties of these materials be developed.

Various aspects of our present understanding of nanostructured materials and their properties have been briefly presented here, along with some thoughts regarding a few future research needs in this area. Based upon what we have learned to date about condensed matter in the nanoscale regime, it appears that the future holds great promise for nanophase materials and that the plasma research community can continue to make important contributions to this challenging new area with so much technological potential.

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