METHOD OF FORMING METALLIC AND CERAMIC THIN FILM STRUCTURES USING METAL HALIDES AND ALKALI METALS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application No. 60/041,965, filed Apr. 3, 1997, and U.S. Provisional Application No. 60/061,443, filed Oct. 9, 1997.

FIELD OF THE INVENTION

The present invention is directed to a method of forming thin film structures using chemical vapor deposition and, in particular, forming thin films by a gaseous-phase reaction between gaseous metal halides and alkali metal gases.

BACKGROUND ART

The worldwide market for Chemical Vapor Deposition (CVD) equipment and services is projected to grow from \$3.5 billion (per year) in 1995 to \$5.4 billion by the year 2000. The two major industrial sectors are: (a) microelectronics which currently accounts for approximately 80% of the market, and (b) surface coatings applications (surface hardness enhancement, corrosion inhibition, and medical) which accounts for the remaining 20% of the market. The microelectronics industry is concerned with stringent purity requirements, while the surface coatings industry is primarily concerned with surface hardening (for machine tooling) and surface coating (for corrosion inhibition and medical applications). While the microelectronics industry can incur a significant expense to produce a high-purity film with exacting electrical performance, many surface enhancement applications cannot tolerate the high production costs typical of the present-day CVD techniques. Additional challenges that both industries face are the expense of disposing of CVD byproducts and the high surface temperature requirement for many conventional CVD processes (900° C. to 1200° C. for thermal CVD of titanium). This latter point is of significance because many substrates may not be capable of accepting high deposition temperatures. For example, mild steel (less than 0.25% C) undergoes a phase transition at elevated temperatures e.g., 723° C., such a change affecting the steel's properties.

Various techniques have been proposed to form thin films using CVD. One technique uses halides such as titanium halide with silanes and ammonia as disclosed in U.S. Pat. No. 5,595,784 to Kaim et al.

In spite of the prior art techniques known to date, a need has developed to provide a CVD process for making thin films on substrates that is low cost, is environmentally benign, uses low temperatures and provides reasonable purity levels. The present invention solves this need by developing a CVD technique that uses a metal-containing halide vapor and an alkali metal vapor to produce a thin film structure.

The generation of bulk titanium by reacting titanium halide vapor and sodium vapor is known. This chemistry has also been demonstrated to be useful for a variety of applications including the synthesis of titanium nanoparticles and TiB_2 nanoparticles, for the formation of an iron/salt magnetic nanocomposites, for the study of phase segregation in binary SiO_2/TiO_2 and SiO_2/Fe_2O_3 nanoparticles, for the synthesis of high purity Si (near photovoltaic grade, and for the remediation of chlorinated fluorocarbons (CFC's))

However, the use of alkali metals, e.g., sodium and potassium, has not been suggested for use in industrial chemical vapor deposition applications primarily because their reductive power is so great that it tends to cause premature and detrimental gas-phase particle precipitation. Furthermore, the deposition of salts is problematic in that high temperatures are required to volatilize the deposited salt.

SUMMARY OF THE INVENTION

Accordingly, it is a first object of the present invention to provide an improved chemical vapor deposition method for making thin films of metals, alloys and ceramic materials.

Another object of the present invention is to provide a low temperature method of chemical vapor deposition.

A still further object of the present invention is to provide a thin film chemical vapor deposition method that suppresses formation of large particles during gas-phase reaction of the method.

One other object of the present invention is to provide an apparatus for making thin film structures.

Yet another object of the invention is a chemical vapor deposition method which produces environmentally benign by-products.

Other objects and advantages of the present invention will become apparent as a description thereof proceeds.

In satisfaction of the foregoing objects and advantages, the present invention, in one mode, demonstrates that a low temperature (600° C.) alkali metal/metal halide reaction can be run at conditions under-saturated in salt, and that a salt-free, low temperatures CVD film can be achieved. The high reductive power of alkali metals such as sodium or potassium now becomes a benefit in that the thermodynamics so strongly favor the production of salt that there is no inherent need to heat the substrate in order to drive the reaction chemistry (as is typically done in many CVD processes). If desired, problematic gas-phase particle formation, and salt deposition can be avoided by using dilute reactant concentrations and moderate substrate temperatures, thereby allowing the production of a salt free film.

In another mode, the invention entails a method of forming a thin film of material on a substrate comprising the steps of providing a first precursor gas comprising an alkali metal and at least one second precursor gas comprising a halide compound gas wherein the halide compound includes at least one component of the material. The first and second precursor gases are reacted under gaseous and vacuum conditions to form the material and deposit the material on the substrate. The first precursor gas can be an alkali metal selected from the elemental group IA consisting of sodium, potassium, rubidium and cesium and the halide compound includes metals, non-metals, semiconductors, and combinations thereof. The metal can be selected from the group of the Group IIIB, IVB, VB, VIB, VIIB, VIIIB, IA, IIA, IIIA, IVA, VA, and VIA elements and combinations thereof. The non-metal or semiconductor can be selected from the groups consisting of IIIA (Boron), IVA (Carbon and Silicon), VA, and VIA. The halide compound includes a halogen element selected from the group VIIA consisting of chlorine, fluorine, bromine and iodine.

The method can further comprise a carrier gas as part of the reacting step wherein the carrier gas can be non-reactive or reactive or a combination of both, e.g., oxygen, nitrogen, argon, helium or the like. The carrier gas can be included as part of the first and second precursor gases or added separate thereto.