Process for the Generation of Metal- or Semimetal-containing Films

Description

The present invention is in the field of processes for the generation of inorganic metal- or semimetal-containing films on substrates, in particular atomic layer deposition processes.

With the ongoing miniaturization, e.g. in the semiconductor industry, the need for thin inorganic films on substrates increases while the requirements on the quality of such films become stricter. Thin metal or semimetal films serve different purposes such as barrier layers, conducting features, or capping layers. Several methods for the generation of metal or semimetal films are known. One of them is the deposition of film forming compounds from the gaseous state on a substrate. In order to bring metal or semimetal atoms into the gaseous state at moderate temperatures, it is necessary to provide volatile precursors, e.g. by complexation of the metals or semimetals with suitable ligands. These precursors need to be sufficiently stable for evaporation, but on the other hand they need to be reactive enough to react with the surface of deposition.

EP 3 121 309 A1 discloses a process for depositing aluminum nitride films from tris(dialkylamino)aluminum precursors. However, the precursor is not stable enough for applications which require high quality films.

In order to convert deposited metal or semimetal complexes to metal or semimetal films, it is usually necessary to expose the deposited metal or semimetal complex to a reducing agent. Typically, hydrogen gas is used to convert deposited metal or semimetal complexes to metal or semimetal films. While hydrogen works reasonably well as reducing agent for relatively noble metals like copper or silver, it does not yield satisfactory results for more electropositive metals such as titanium or aluminum.

WO 2013 / 070 702 A1 discloses a process for depositing metal films employing aluminum hydride which is coordinated by a diamine as reducing agent. While this reducing agent generally yields good results, for some demanding applications, higher vapor pressures, stability and/or reduction potential is required.

D. Mukherjee et al. disclose in Chemical Communications, volume 53 (2017) page 3493-3496 alane complexes with a chelating ligand. However, its suitability for preparing inorganic metal- or semimetal-containing films is not recognized by the authors as the compound is only used for organic synthesis in solution.

It was therefore an object of the present invention to provide a process for preparing inorganic metal- or semimetal-containing films having less impurity in the film. The process materials should be easy to handle; in particular, it should be possible to vaporize them with as little decomposition as possible. Further, the process material should not decompose at the deposition surface under process conditions but at the same time it should have enough reactivity to partic-

Furthermore, it is possible to expose the deposited compound of general formula (I), (II), or (III) to a plasma like an oxygen plasma, hydrogen plasma, ammonia plasma, or nitrogen plasma; to oxidants like oxygen, oxygen radicals, ozone, nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxde (NO_2) or hydrogen peroxide; to ammonia or ammonia derivatives for example tert-butylamine, iso-propylamine, dimethylamine, methylethylamine, or diethylamine; to hydrazine or hydrazine derivatives like N,N-dimethylhydrazine; to solvents like water, alkanes, or tetrachlorocarbon; or to boron compound like borane. The choice depends on the chemical structure of the desired layer. For aluminum oxide, it is preferable to use oxidants, plasma or water, in particular oxygen, water, oxygen plasma or ozone. For aluminum, nitride, ammonia, hydrazine, hydrazine derivatives, nitrogen plasma or ammonia plasma are preferred. For aluminum boride boron compounds are preferred. For aluminum carbide, alkanes or tetrachlorocarbon are preferred. For aluminum carbide nitride, mixtures including alkanes, tetrachlorocarbon, ammonia and/or hydrazine are preferred.

The process is preferably performed as atomic layer deposition (ALD) process comprising the sequence
(c) bringing a solid substrate in contact with a compound of general formula (I), (II), or (III) and
(d) decomposing the adsorbed compound of general formula (I), (II), or (III). Preferably, the sequence comprising (c) and (d) is performed at least twice, more preferably at least five times, even more preferably at least 10 times, in particular at least 50 times. Often, the sequence comprising (c) and (d) is performed not more than 1000 times.

In this case the temperature of the substrate is preferably 5 °C to 40 °C higher than the place where the metal- or semimetal-containing compound is brought into the gaseous state, for example 20 °C. Preferably, the temperature of the substrate is from room temperature to 400 °C, more preferably from 100 to 300 °C, such as 150 to 220 °C.

If the temperature of the substrate in the process according to the present invention is kept below the decomposition temperature of the metal- or semimetal-containing compound, typically a monolayer is deposited on the solid substrate. Once a molecule of the metal- or semimetal-containing compound is deposited on the solid substrate further deposition on top of it usually becomes less likely. Thus, the deposition of the metal- or semimetal-containing compound on the solid substrate preferably represents a self-limiting process step. The typical layer thickness of a self-limiting deposition processes step is from 0.01 to 1 nm, preferably from 0.02 to 0.5 nm, more preferably from 0.03 to 0.4 nm, in particular from 0.05 to 0.2 nm. The layer thickness is typically measured by ellipsometry as described in PAS 1022 DE (Referenzverfahren zur Bestimmung von optischen und dielektrischen Materialeigenschaften sowie der Schichtdicke dünner Schichten mittels Ellipsometrie; February 2004).

The exposure of the substrate with the compound of general formula (I), (II), or (III) or the metal- or semimetal-containing compound can take from milliseconds to several minutes, preferably from 0.1 second to 1 minute, in particular from 1 to 10 seconds. The longer the solid substrate at a temperature below the decomposition temperature of the compound of general formula (I),