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SVC Topics

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PVD Processes: Plasma-enhanced Chemical Vapor Deposition (PECVD)

hemical Vapor Deposition (CVD) C is the deposition of atoms or molecules by the reduction or decomposition of a chemical vapor precursor species, which contains the material to be deposited. Reduction is normally accomplished by hydrogen at an elevated temperature. Decomposition is accomplished by thermal activation. In conventional thermal CVD processing, the precursor vapor is partially heated in the gas phase and finally heated in contact with the hot surface of the substrate. A plasma can be used to aid in reducing or decomposing the precursor vapor and allows reduction or deposition at temperatures lower than that required for strictly thermally driven processes.

The deposited material may react with other gaseous species in the system to give compounds or glasses (oxides, nitrides, oxynitrides) and these are called synthesis reactions. CVD processing is often accompanied by hot volatile reaction byproducts, such as H_2 , Cl_2 , HCl, H_2O or HF, and those, along with unused precursor vapors and other processing gases, must be removed by the pumping system.

CVD has numerous other names, such as vapor phase epitaxy (VPE), when CVD is used to deposit singlecrystal films; metalorganic CVD (MOCVD), when the precursor gas is a metalorganic species; plasma enhanced CVD (PECVD), when a plasma is used to induce or enhance decomposition; and reaction and lowpressure CVD (LPCVD), when the pressure is less than ambient. With some types of precursor vapors, such as organic monomers or the siloxanes, the deposited material may be in the form of polymeric chains and the process is called plasma polymerization. CVD can be used to deposit elements, alloys, glasses, compounds and organic or inorganic polymeric materials.

Most CVD processing is done at atmospheric pressure (atmospheric pressure CVD—APCVD) after the CVD system has been evacuated to remove unwanted gases and backfilled with the processing gases. Heating of the sub-

strate, precursor vapors and reactive gases is an important process variable. The heating is done either by having a hot surface, usually holding the substrates, immersed in the gas (cold wall reactor) or by having the deposition chamber contained in a furnace (hot wall reactor). The gas flow rate and flow pattern are often important process variables. The concentration of the precursor vapors and reactive gas(es) is an important process parameter, and often inert carrier gases (diluents) are used to establish the concentration of the processing gases. Because the surface to be coated is immersed in the vapor, the deposition is over the entire surface, but the thickness and microstructure of the deposit may



A parallel plate rf-driven PECVD reactor.

vary as a result of flow and heating patterns. If the deposition temperature is not sufficiently high, the precursor may not be completely dissociated. In depositing silicon from $SiCl_4$, for example, there may be some chlorine retained in the deposited material if the deposition temperature is too low.

CVD Reactions

Some CVD reactions are (equations are unbalanced):

 $\begin{array}{l} Decomposition \ reactions \\ \mathrm{Ni}(\mathrm{CO})_4 \longrightarrow \mathrm{Ni} + \mathrm{CO}_2 \\ \mathrm{SiH}_4 \longrightarrow \mathrm{Si} + \mathrm{H}_2 \\ \mathrm{B}_2\mathrm{H}_6 \ \mathrm{or} \ \mathrm{BCl}_3 \longrightarrow \mathrm{B} + \mathrm{H}_2 \ \mathrm{or} \ \mathrm{Cl}_2 \\ \mathrm{CH}_4 \longrightarrow \mathrm{C} + \mathrm{H}_2 \end{array}$

Reduction reactions WF₆ + H₂ \longrightarrow W + HF SiCl₄ \longrightarrow Si + HCl TiCl₄ + H₂ \longrightarrow Ti + HCl

 $\begin{array}{l} Synthesis \ reactions\\ TiCl_4 + CH_4 \longrightarrow TiC + HCl\\ SiH_4 + O_2 \longrightarrow SiO_2 + H_2\\ SiH_4 + NH_3 \longrightarrow Si_3N_4 + H_2\\ WF_6 + C_2H_2 + H_2 \longrightarrow W_2C + HF\\ TiCl_4 + NH_3 \longrightarrow TiN + HCl \end{array}$

In low-pressure CVD (LPCVD), the gas concentration can be controlled by the gas pressure, as well as by the addition of carrier gases. At low pressures, heating of the gases and vapors occurs mostly on the hot surfaces. At low pressures, the use of a plasma (plasma-enhanced CVD-PECVD) allows the fragmentation of the precursor species to begin in the gas phase, and the plasma allows the activation of reactive gases to make them more chemically reactive with the deposited material. Deposition may be done in the plasma generation region (direct plasma system) with the substrates on an electrode or away from the plasma generation region (downstream or remote plasma system).

The use of an rf-driven plasma allows the plasma to be formed in a large volume between the electrodes. The figure shows a parallel plate, rfdriven PECVD reactor (Reinberg reactor) that is commonly used in semiconductor processing. Some typical process parameters for this type of reactor are: RF-50 kHz to 13.56 MHz, 1kW rf power, pressure down to 2 Torr, gas flow 200 sccm and substrate temperature 25 °C to 700 °C.

Some PECVD reactions and the materials deposited are (equations not balanced):

$$\label{eq:WF_6+SiH_4-230 °C-} \begin{split} & \text{WF_6+SiH_4-230 °C-} > \text{tungsten} \\ & \text{silicide (WSi)} \\ & \text{TaCl_5+SiH_2Cl_2+H_2-580 °C-} > \\ & \text{tantalum silicide (TaSi_2)} \end{split}$$

In the semiconductor industry, films deposited by PECVD processing are often subsequently heat treated to a high temperature (postdeposition anneal).

Any plasma will aid in decomposing a chemical vapor precursor. At low pressures, such as are used in PVD processing (<15 mTorr), PECVD (LP-PECVD) can be used in conjunction with PVD processes of vacuum evaporation, sputter deposition or arc vapor deposition, to give a hybrid deposition process (PVD/LP-PECVD). In PVD/LP-PECVD processing, the most commonly used chemical vapor precursors are acetylene (C_2H_2) and methane (CH_4) to provide carbon for reactively depositing carbides and carbonitrides. Typically, concurrent high energy ion bombardment (ion plating) is used to facilitate the chemical reaction. In LP-PECVD, the plasma is usually established using an unbalanced

magnetron configuration often in a dual cathode or pulsed DC arrangement. In some cases an arc plasma is used.

In LP-PECVD of carbon, gas phase decomposition and vapor phase nucleation can produce very fine carbon particles ("ultrafine particles" or "soot"). In the plasma, these particles become negatively charged. If a surface is at a high negative potential with respect to the plasma, such as in ion plating, the particles do not deposit on that surface. In the carbon LP-PECVD system, the vacuum pumping system must be able to handle these particulates.

Low-pressure CVD, in particular PECVD and LP-PECVD, is an important vacuum deposition process either by itself or as part of a hybrid deposition process. PRSF

Bibliography

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