ABSTRACT

EXPERIMENTAL INVESTIGATIONS OF THERMODYNAMIC PROPERTIES OF ORGANOMETALLIC COMPOUNDS

Organometallic compounds are often volatile enough to be useful as precursors of the metals in vapor phase deposition process, e.g. chemical vapor deposition (CVD). For this process the precursor molecules are evaporated. To engineer such a process the knowledge of the vapor or sublimation pressures is essential because they determine the maximum theoretical growth rate and the composition. The gaseous diffusion coefficients for organometallic compounds are needed for the calculation of the Sherwood and Lewis numbers used to describe mass transfer process. Such data are either lacking or not well established.

This work reports the thermal stability, vapor pressure and the gaseous diffusion coefficient for numerous organometallic compounds that are used as CVD precursors. These includes

1. Metal acetylacetonates ($[M(acac)_n]$) of aluminium, chromium, iron, thulium, manganese, ruthenium, vanadium, dysprosium, zinc, copper and nickel.
2. Metal 2,2,6,6-tetramethyl-3,5-heptandionate ($[M(tmhd)_n]$) of iron, manganese, aluminium, chromium, europium, nickel, and copper.
3. Metallocene ($[M(cp)_n]$) of nickel and ruthenium.
4. Newly synthesized precursors or non commercial precursors of hafnium, zirconium, ruthenium, tungsten and copper.

Some of the precursors were sensitive towards ambient atmosphere. Therefore, the samples were stored in the glove box. The thermogravimetry analyser (TGA) apparatus was also kept inside the glove box so that an inert atmosphere is always present during handling of the sample. Non isothermal as well as isothermal thermogravimetry was used to study the thermal stability of the precursors. Due attention was being paid to the agreement of the mass loss curve with the theory and the amount of residue. If nearly linear mass loss curve was obtained along with the negligible amount of residue, the substance was considered to be thermally stable. It was then subjected to vapor pressure measurement using a Knudsen cell. A special arrangement was made into the experimental setup to ensure the circulation of nitrogen to prevent the degradation of the sample due to atmospheric air during the heating period. The vapor pressures from 0.01-25 Pa were measured with the Knudsen cell in the temperature range of 317-442K.

The gaseous diffusion coefficients were determined using the TGA. The TGA method of the determination of the gaseous diffusion coefficient is based on the fact that the mass transfer rate at a given total pressure and temperature is mainly a function of the diffusion coefficient and the vapor pressure of the sublimating substance. The vapor pressures determined using the Knudsen cell were combined with the TGA measurements to obtain the diffusion coefficients. The gaseous diffusion coefficients for the organometallic compounds have been reported for the first time.

Apart from the organometallic compounds experiments have been performed with two well studied substances anthracene and pyrene to check the present approach. The measured value of vapor pressure and the gaseous diffusion coefficient values were in good agreement with all the available literature values for these reference substances.