THERMODYNAMIC STUDY OF MIXED LIGAND COBALT Β-DIKETONATE COMPLEXES AND THEIR IMPLICATIONS FOR Co-OXIDE THIN FILM DEPOSITION

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Co-oxide thin films exhibit semiconducting properties, rendering them relevant for applications in optics and electronics as well as for secondary electron emission composite materials. To obtain these films using chemical vapor deposition (MOCVD), active development of volatile precursors is underway. Cobalt(II) β-diketonate complexes could be promising precursors provided that mononuclear derivatives are stabilized by additional neutral ligands to precise control the vapor mass-transport during deposition process. However, the library of such complexes is limited, and even for known precursors like $Co(tmeda)(hfac)_2$ and $Co(tmeda)(acac)_2$ (tmeda = N,N,N',N'-tetramethylethylenediamine, hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionato, acac = pentane-2,4-dionato) there is a lack of quantitative data on thermochemical properties.

Here, the library of mixed ligand cobalt β-diketonate complexes $Co(tmeda)(L)_2$ for MOCVD application has been supplemented by three new fluorinated derivatives (L = pfpac (5,5,6,6,6-pentafluorohexane-2,4-dionato), hfbac (5,5,6,6,7,7,7-heptafluoroheptane-2,4-dionato), ofhac (3H,3H-octafluorohexane-2,4-dionato)). The structural features and thermochemical properties of these complexes and their closed analogues $Co(tmeda)(hfac)_2$ and $Co(tmeda)(acac)_2$ have been studied. The structures of $Co(tmeda)(hfbac)_2$, $Co(tmeda)(ofhac)_2$ and one new phase of $Co(tmeda)(hfac)_2$ have been revealed. The information on the condensed phase transitions for $Co(tmeda)(L)_2$ has been obtained. A characteristic feature of the complex with L = pfpac is its retarded crystallization and glass-forming ability.

The temperature dependence of saturated vapor pressure for $Co(tmeda)(hfac)_2$ was determined allowing us to develop MOCVD process of Co oxide films with controlled mass transport of precursor at the evaporator temperature range 333-353 K. This provides the optimal conditions for growth hexagonal CoO or Co_3O_4 films. The Co oxide films exhibit a minimal impurity level on C, F elements and no traces of N that makes them appropriated for different applications. The $Co(tmeda)(acac)_2$ has been tested to obtain Co_3O_4 films without F impurities. The influence of the oxygen flow rate and deposition temperatures parameters on the composition, morphology and thickness of Co oxide films deposited from these precursors has been determined.

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