THERMODYNAMIC STUDY OF VOLATILE Ru(II) AND Co(I) CYCLOPENTADIENYL DERIVATIVES

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To improve the electrical parameters of integrated circuits, modifications to the circuit architecture are essential, including reductions in the size of metal lines. In this case replacing traditional Cu with other conductive materials such as Ru and Co is required. Atomic layer deposition (ALD) is the method of choice for producing such films due to the most precise possibilities of thickness control and conformality.

To be applied to ALD, the metal precursors must be highly volatile, thermally stable, and highly reactive towards to surface groups of the substrate and gas-co-reagent. Liquid precursors as $Ru(^{Et}Cp)_2$ and $Co(CO)_2Cp$ (Cp is cyclopentadienyl, ^{Et}Cp is ethylcyclopentadienyl), are effective for obtaining metal layers. Data on their thermal properties are limited. For $Ru(^{Et}Cp)_2$, the available volatility data were measured indirectly while the gas phase composition was not controlled [1]. For $Co(CO)_2Cp$ there are only data on vapor pressure in a single point [2]. To supply and verify these data, the current work was devoted to the comprehensive thermodynamic of $Ru(^{Et}Cp)_2$ and $Co(CO)_2Cp$ ALD precursors.

According to DSC, both compounds are thermally stable in the condensed phase over wide temperature ranges up to 393 K and 473 K for $Co(CO)_2Cp$ and $Ru(^{Et}Cp)_2$, respectively. The thermodynamic characteristics of melting were first determined to be: *m.p.* = 256.4±0.5 K, $\Delta_{melt}H_{m.p.}$ = 12.7±0.6 kJ/mol for $Co(CO)_2Cp$ and *m.p.* = 274.2±0.5 K, $\Delta_{melt}H_{m.p.}$ = 22.9±0.5 kJ/mol for $Ru(^{Et}Cp)_2$. The saturated vapor pressures over the liquid precursors have been measured by the static method with a membrane-gauge manometer within wide temperature intervals: 293–399 K for $Co(CO)_2Cp$ and 369–462 K for $Ru(^{Et}Cp)_2$. Also, the thermodynamic parameters of precursor's evaporation were determined: $\Delta_{vap}H_{346}$ = 44.4±0.3 kJ/mol, $\Delta_{vap}S_{346}$ = 98.4±0.9 J/mol·K for $Co(CO)_2Cp$ and $\Delta_{vap}H_{420}$ = 59.3±0.9 kJ/mol, $\Delta_{vap}S_{420}$ = 103.5±2.3 J/mol·K for $Ru(^{Et}Cp)_2$. Unsaturated vapor pressure measurements confirmed the monomolecular nature of the vapor composition. Thus, the obtained data provide a suitable basis for selecting evaporation temperature parameters in ALD processes.

1. Website of Kojundo Chemical Laboratory CO., LTD: official website. URL: https://www.kojundo.co.jp/dcms_media/other/Ru_EtCp_2_EN.pdf

2. Kaloyeros A.E., Y. Pan, J. Goff, B. Arkles. Cobalt Thin Films: Trends in Processing Technologies and Emerging Applications // ECS J. Solid State Sci. Techn. 2019. Vol 8(2). P119-P152.

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