Measurements of Metal Alkylamide Density during Atomic Layer Deposition Using a Mid-Infrared Light-Emitting Diode (LED) Source

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Abstract

A nondispersive infrared (NDIR) gas analyzer that utilizes a mid-infrared light emitting diode (LED) source was demonstrated for monitoring the metal alkylamide compound tetrakis(dimethylamido) titanium (TDMAT), Ti[N(CH3)2]4. This NDIR gas analyzer was based on direct absorption measurement of TDMAT vapor in the C–H stretching spectral region, a spectral region accessed using a LED with a nominal emission center wavelength of 3.65 μm. The sensitivity of this technique to TDMAT was determined by comparing the absorbance measured using this technique to the TDMAT density as determined using in situ Fourier transform IR (FT-IR) spectroscopy. Fourier transform IR spectroscopy was employed because this technique could be used to (1) quantify TDMAT density in the presence of a carrier gas (the presence of which precludes the use of a capacitance manometer to establish TDMAT density) and (2) distinguish between TDMAT and other gasphase species containing IR-active C–H stretching modes (allowing separation of the signal from the LED-based optical system into fractions due to TDMAT and other species, when necessary). During TDMAT-only delivery, i.e., in the absence of co-reactants and deposition products, TDMAT minimum detectable molecular densities as low as ≈4×10^{12} cm^{-3} were demonstrated, with short measurement times and appropriate signal averaging. Reactions involving TDMAT often result in the evolution of the reaction product dimethylamine (DMA), both as a thermal decomposition product in a TDMAT ampoule and as a deposition reaction product in the deposition chamber. Hence, the presence of DMA represents a significant potential interference for this technique, and therefore, the sensitivity of this technique to DMA was also determined by measuring DMA absorbance as a function of pressure. The ratio of the TDMAT sensitivity to the DMA sensitivity was determined to be ≈6.0. To further examine the selectivity of this technique, measurements were also performed during atomic layer deposition (ALD) of titanium dioxide using TDMAT and water. During ALD, potential interferences were expected from the evolution of DMA due to deposition reactions and the deposition on the windows of species containing IR-active C–H stretching modes. It was found that the interfering effects of the evolution of DMA and deposition of species on the windows corresponded to a maximum of only ≈6% of the total observed TDMAT density. However, this level of interference likely is relatively low compared to a typical chemical vapor deposition process in which co-reactants are introduced into the chamber at the same time.

Keywords Atomic layer deposition, ALD, Infrared absorption, Light emitting diode, LED, Metal alkylamide, Nondispersive infrared gas analyzer, NDIR, Tetrakis(dimethylamido) titanium, TDMAT