

Interaction of Magnesocene (MgCp_2) and Ammonia (NH_3) Explains “Memory Effects” during p-Type Doping of Group-III Nitrides

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Motivation—Magnesocene [$\text{Mg}(\text{C}_5\text{H}_5)_2 = \text{MgCp}_2$] is the dominant precursor used for the p-type doping of GaN and its alloys in the AlGaInN system (III-nitrides). Unfortunately, difficulties remain with predictably controlling the incorporation of Mg during metal organic chemical vapor deposition (MOCVD) film growth, which often exhibits poorly understood “memory effects.” The electron deficiency of the Mg center in MgCp_2 suggests that it may be susceptible to nucleophilic attack by NH_3 , resulting in the formation of condensable Lewis acid-base complexes (adducts). An improved understanding of the interaction between MgCp_2 and NH_3 could shed light into the p-type doping issues.

Accomplishment—We have determined, for the first time, the details of the interaction between magnesocene and ammonia using a combined experimental and theoretical approach. Our results show that at room temperature MgCp_2 and NH_3 react to form the complexes $\text{NH}_3:\text{MgCp}_2$ and $(\text{NH}_3)_2:\text{MgCp}_2$. The formation and subsequent condensation of these low vapor pressure adducts is the probable source of parasitic Mg loss that results in the observed unpredictable Mg incorporation and slow turn-on and turn-off response during p-type doping of III-nitrides (i.e., the so-called memory effects).

The interaction between MgCp_2 and NH_3 at room temperature was investigated by FTIR spectroscopy and density functional theory (DFT) quantum chemistry calculations. Figure 1 summarizes the model developed, which is consistent with the observed and calculated chemistry. Upon mixing, MgCp_2 and NH_3 can

undergo complexation to form a “1:1” $\text{NH}_3:\text{MgCp}_2$ adduct, which is calculated to have a binding energy of 5.4 kcal/mol (relative to the reactants). We calculated only a minor energy barrier to formation of 1.0 kcal/mol, indicating that the reaction should be facile at room temperature. Interestingly, the 1:1 adduct can undergo further complexation with a second NH_3 molecule to form a more stable “2:1” $(\text{NH}_3)_2:\text{MgCp}_2$ adduct. The 2:1 adduct has a binding energy of 12.3 kcal/mol and no significant energy barrier to form. Thus, equilibrium exists between MgCp_2 , NH_3 , and the 1:1 and 2:1 adducts which is dependent on the process conditions. We have confirmed this using *in situ* infrared spectroscopy experiments. Figure 2 shows the IR spectra of the 1:1 and 2:1 adducts condensed on a KCl window at room temperature, which can be isolated at low and high pressure (or NH_3 concentration), respectively. The calculated spectra for the complexes (overlaid as bars) show good agreement with the experimental data. Formation of both the condensable 1:1 and 2:1 adducts was found to be completely reversible at room temperature.

Significance—Due to our improved understanding of the interaction between MgCp_2 and NH_3 , intelligent efforts to eliminate or minimize condensable adduct formation can now be undertaken. These efforts should lead to improvements in reactor design and performance with regards to the crucial issue of controlled p-type doping of III-nitride materials. This work was recently featured on the cover of, and as an article within, *The Journal of Physical Chemistry A* (June 3, 2004).

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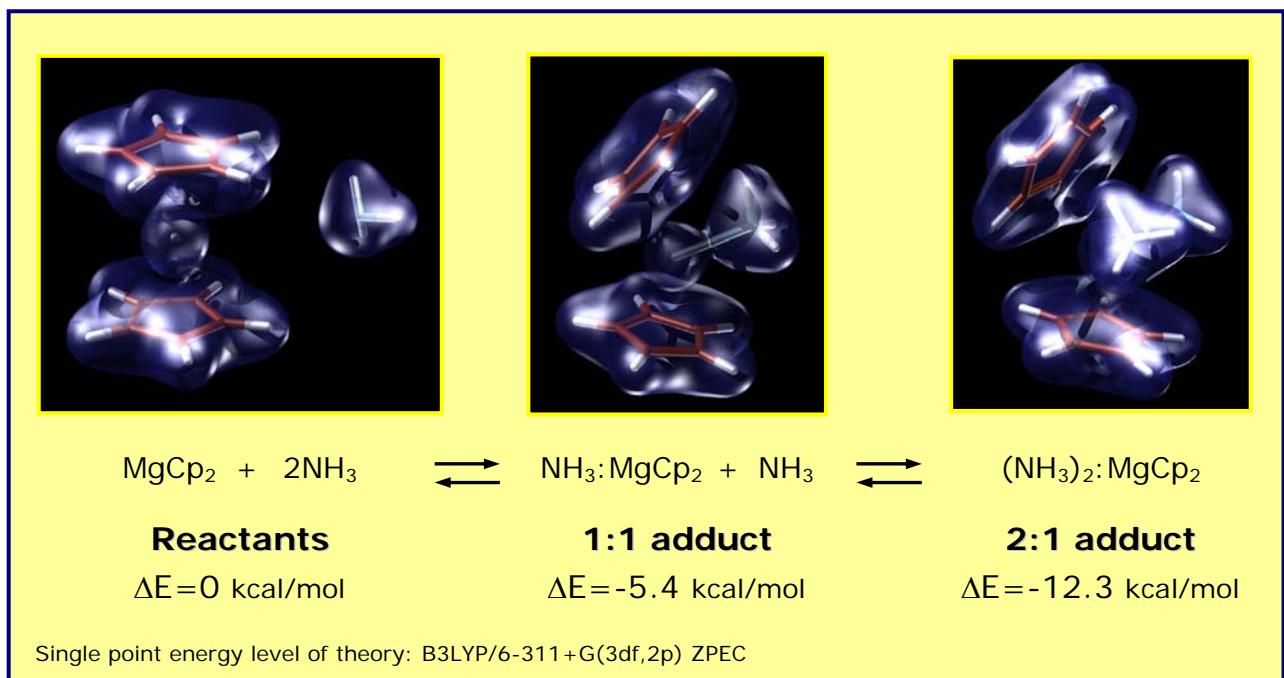


Figure 1. Model summarizing the interaction between magnesocene and ammonia, shown with calculated optimized geometries and energetics.

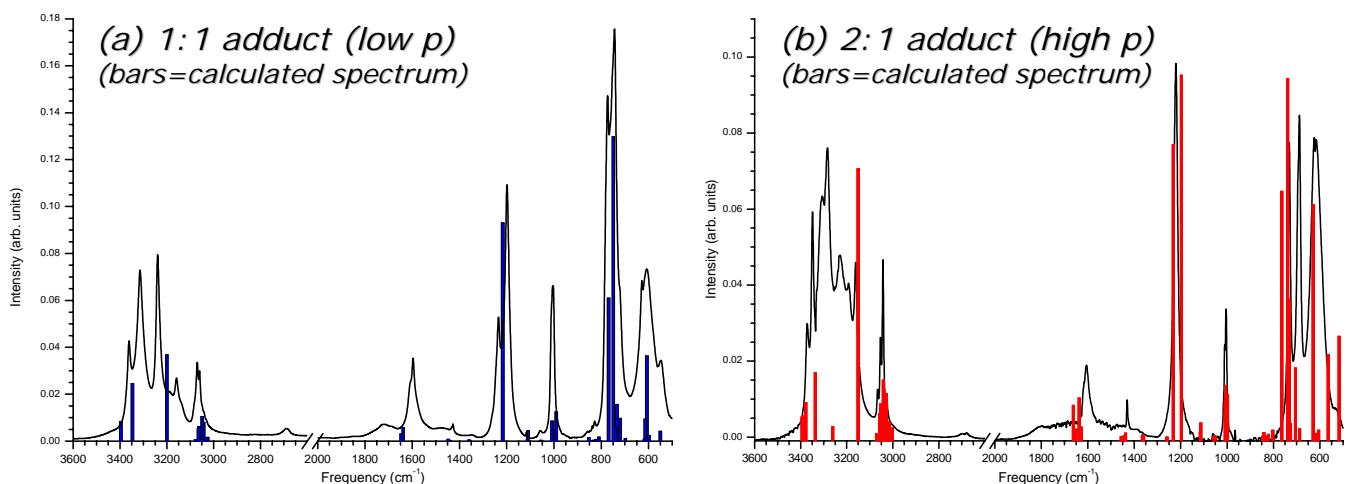


Figure 2. IR spectra of the condensed (a) 1:1 adduct and (b) 2:1 adduct at room temperature, with calculated spectra overlaid (bars).