Excimer Laser Photolysis of Zn Dialkyls for Zn Deposition.

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Summary. — Excimer laser-induced photochemistry of dimethylzinc (DMZn) and diethylzinc (DEZn) has been investigated by multiphoton ionization time-of-flight mass spectroscopy. After the results achieved, DEZn was chosen as precursor compound for zinc film photodeposition. The organometallic was photolyzed by a focussed KrF excimer laser beam perpendicularly impinging onto a quartz substrate. Localized zinc deposition with thicknesses in the range (300 - 3000) Å has been obtained and the deposition process has been investigated by monitoring the time evolution of the fraction of a He-Ne laser beam transmitted by the growing zinc film.

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1. — Introduction.

Low-temperature laser-induced CVD of metallic films from gaseous organometallic precursors is very attractive for microelectronic device fabrication (1).

In particular Zn deposition is useful for several applications ranging from GaAs (2) and InP (3) doping to ZnO (4) and Zn-containing binary semiconductor compound (5) growth.

Investigation of zinc dialkyl photochemistry helps in identifying the ideal experimental conditions for achieving optimal film growth rate and characteristics of the deposited material.

2. – Excimer laser photolysis of Zn dialkyls monitored by tunable dye-laser ionization mass spectroscopy.

Dimethyl alkyls containing II B metals (Me = Zn, Cd, Hg) have a linear structure with the CH₃ groups freely rotating around the Me-C bonds. After an ab initio calculation of the Cd(CH₃)₂ electronic ground state, these organometalllics can be considered linear three-centre molecules and described in the scheme of the much simpler bivalent metal dihydrides MeH₂, which are taken as having a ground linear structure and assuming bent configurations in some excited electronic states; furthermore, since the bonding orbital arrangement is not altered by the replacement of methyl with ethyl ligands, the same quasi-triatomic picture can be assumed also in the case of the diethyl metal alkyls.

Figure 1 reports the linear UV absorption spectra of dimethylzinc (DMZn) Zn(CH₃)₂ and diethylzinc (DEZn) Zn(C₂H₅)₂. As can be easily seen, both spectra show a broad absorption feature (centred around 49 000 cm⁻¹ in the case of DMZn and around 45 000 cm⁻¹ in the case of DEZn), exhibiting a structured profile followed by a smooth tail in the low-energy side.

A careful analysis has assigned the long-wavelength continuum to a linear-bent transition from the ground X¹Σ⁺ to the first excited electronic state A¹A₁ of the molecule and the structured band to a linear-linear transition from the ground to the second electronic excited state B¹Πₓ. The two transitions are both dissociative and cause the elimination of a methyl group from DMZn; however, whereas the bent channel A¹A₁ starting from 39 000 cm⁻¹ produces a monomethyl fragment in its ground electronic state, the transition to the linear B¹Πₓ state induced above 46 000 cm⁻¹ gives a monomethyl fragment containing the metal excited at its first atomic level.

On the basis of the strong similarities shown either by the DMZn and DEZn molecular structure or by their linear spectra, it is reasonable to assign the DEZn absorption features centred at 45 000 cm⁻¹ to two electronic dissociative transitions as in the case of DMZn, originating a monoethyl Zn(C₂H₅) and a C₂H₅ fragment through a bent (starting from 36 000 cm⁻¹) or through a linear (above 41 000 cm⁻¹) channel.