THE VAPOR PHASE INTERACTION OF TRIMETHYLALUMINUM WITH GRAPHITE DURING OMVPE

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RESUME : Nous avons étudié l'interaction de $(CH_3)_3Al$ avec les surfaces de graphite en utilisant un spectrometre de masse à jet moléculaire. Nos résultats indiquent un effect d'adsorption important qui explique des phénomènes observés pendant la croissance organométallique de $Al_xGa_{1-x}As$ comme des transitions lentes de la concentration d'aluminium, et la réduction de l'incorporation d'oxygène et de sélénium.

ABSTRACT : We have used a molecular beam mass spectrometer to study the interaction of trimethylaluminum (TMA) with graphite surfaces. Our results indicate that a strong adsorption effect occurs which explains phenomena occuring during OMVPE growth of $Al_xGa_{1-x}As$, such as long Al transients, oxygen gettering, and reduced incorporation of selenium.

I. INTRODUCTION: Highly purified, fine-grained graphite has often been a preferred construction material for vapor phase epitaxial reactors because of its thermal and chemical stability as well as the ease with which it can be formed into complex geometries. In addition, Stringfellow and Hom recently found that in the special case of organometallic vapor phase epitaxy (OMVPE) of $Al_xGa_{1-x}As$, the use of graphite baffles upstream of the reaction zone results in a dramatic increase in the observed photoluminescence, apparently by providing a surface where the heterogenous reaction between trimethylaluminum (TMA) and residual oxygen-containing species can occur, thus "gettering" them from the vapor phase[1]. The secondary ion mass spectrometry (SIMS) results of Kisker et al. confirmed this gettering effect of graphite baffles[2].

Despite the advantages of using graphite baffles for reduction of residual oxygen, recent results have indicated that there are perhaps other, less desirable aspects of the chemical activity which results in this gettering ability. In particular, during some attempts to produce double-heterostructure (DH) lasers, very long transients in aluminum concentration have prevented the attainment of very thin

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active layers[3], and a reduction of the doping efficiency of selenium in $Al_xGa_{1-x}As$ have been observed when graphite baffles are used[4]. Finally, Kisker et al. observed that the efficiency of the oxygen gettering effect seemed to be reduced at long times[2], limiting the baffles' usefulness. In the present work, we use a molecular beam mass spectrometer (MBMS) to study the graphite-TMA interaction, and thereby demonstrate that all of these phenomena can be explained by a strong adsorption of TMA onto graphite.

II. EXPERIMENTAL: For this work, we used a mass spectrometer specially designed for the study of vapor phase ambients such as might be found during VPE growth. In this system, which has been previously described in detail, the sampled gases are rapidly expanded through an orifice into a conical nozzle, where a molecular beam of the sampled species is formed and directed toward a quadrapole mass analyzer[5]. The sensitivity of the apparatus is of the order of a few parts per million for most species, and a particular advantage is the rapid sampling time ($\sim 10^{-3}$ sec) which results in the ability to easily study typical vapor phase transients, such as occur in conventional VPE systems.

In this work, we shall briefly summarize the results of our previous measurements of the graphite-TMA interaction[6] before turning to the more important aspects of the effect upon epitaxial growth. Our molecular beam mass spectrometer is situated such that it samples the effluent gas from a reaction chamber. This chamber can be heated and for the study of the interaction of TMA with graphite, strips of graphite are placed inside. We have found that with an empty reaction chamber, the response of the system to a change in gas input concentration is limited only by the propagation of the concentration pulse through the reaction chamber. Diffusion of the gaseous species during this time results in "smearing" of a step change in gaseous concentration. The presence of adsorbing surfaces in the reaction chamber results in a lengthening of the increasing and decreasing transients of a TMA pulse as shown in Fig. 1. In the following, we will derive a relationship between the "integrated desorption", represented by the shaded area of the desorption curve, and the total amount of adsorbed material at steady-state.

To begin, we assume that the desorption process is controlled by a Langmuir type process[7], in which the rate of change in surface coverage is proportional to the amount of remaining surface coverage, θ. In this case the desorbing flux, J_d,
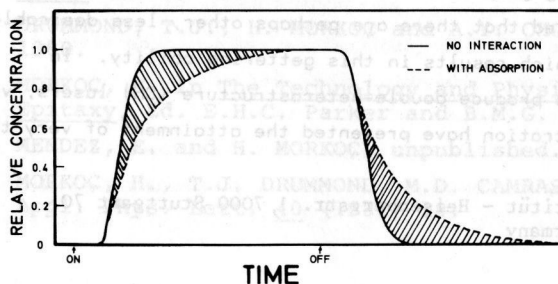
EFFECT OF ADSORPTION ON TMA PULSE

Fig. 1: Effect of adsorption on TMA pulse as measured by MBMS.

is given by Eq. 1:

$$J_d(t) = \frac{k_d \theta_o N_T}{N_{av}} \exp(-k_d t)$$ (1)

where θ_o is the steady-state fraction of surface coverage before the beginning of the desorption transient, k_d is a constant related to the desorption rate, N_T is the surface density of adsorption sites and N_{av} is Avogadro's number. The time-dependent desorption flux is the difference between the transient measured in the presence of graphite or other adsorbing surface, and the reference transient measured with no graphite present. Thus, an expression for the shaded area in Fig. 1 is obtained by integration of Eq. 1:

$$I = \int_o^\infty J_d(t)dt = \frac{\theta_o N_T}{N_{av}}$$ (2)

where I represents the integrated desorption. From this expression, we obtain a value for the amount of steady-state adsorption, given by $\theta_o N_T$. For low coverages, we expect θ_o to be a function of temperature[7] according to Eq. 3,

$$\theta_o \propto \exp\left[\frac{E_{ads}}{RT}\right]$$ (3)

Then, from Eq. 2, the integrated desorption will exhibit the same exponential inverse temperature dependence.

III. RESULTS: We utilized the MBMS system to observe decreasing TMA transients while varying the amount of graphite, the flow rates and the temperature of the reaction chamber. In order to be sure that the observed results were actually caused by the adsorption to TMA, we did similar experiments at various temperatures with inert gases and quartz strips instead of graphite. Only when TMA and graphite were present together did we observe the lengthened transients characteristic of adsorption. Typical results, in Fig. 2, show the strong temperature dependence of the desorption process. In Fig. 3, we present the results of the complete set of measurements of the integrated desorption from graphite as a function of inverse temperature and observe the agreement to the expected exponential dependence. From this data, a value of the energy of adsorption is found to be 15.7 kcal/mole. This value is relatively high, indicating the attachment of TMA to graphite is of a chemical nature[7]. We note that the range of densities of TMA adsorbed to the graphite, $10^{15} - 10^{17} cm^{-2}$, is of the same magnitude as the estimated density of gettered oxygen on graphite, $3 \times 10^{16} cm^{-2}$, reported by Kisker et al.[2]

IV. DISCUSSION: Our results have shown the existence of a strong adsorption effect of TMA to graphite. This provides a source and sink for TMA during OMVPE growth, resulting in slow Al concentration transients in the solid layers and providing a
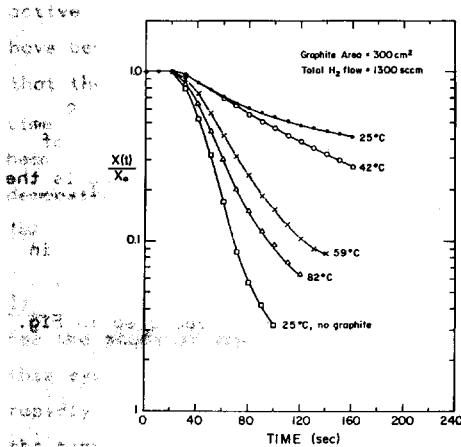
Fig. 2: Experimental measurement of variation of desorption transients as a function of graphite temperature.
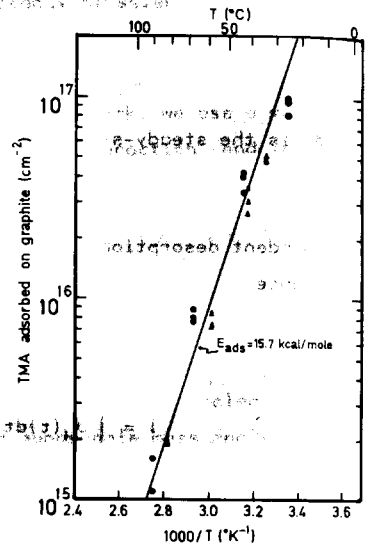
Fig. 3: Adsorbed TMA vs. 1000/T. (●) data taken with 150 cm^2 of graphite in reaction chamber; (▲) data taken with 300cm^2 present.

surface where gettering reactions can occur. In the following, we investigate the impact of these phenomena on OMVPE $Al_xGa_{1-x}As$ layers.

The calculated effect of the adsorption and desorption of TMA from graphite on one Al-profile dependent process, the active layer growth of a DH laser, is shown in Fig. 4. In the case that there is no TMA adsorption, the TMA flow is reduced and the transient can occur sufficiently quickly so that the active layer Al concentration can be controlled to any chosen value. In actual growth systems with graphite baffles, the minimum attainable active layer Al concentration may be relatively high due to slow TMA transients as also shown in Fig. 4. Previously measured Al concentration profiles of layers grown under such conditions appear qualitatively very much the same as in this calculation[3]. One proposed solution to this problem is to completely interrupt the growth by turning off the flow of both the TMA and TMG, letting the reactor purge, and then growing the active layer with the reduced TMA concentration. Also shown in Fig. 4 is the experimentally measured result of such a layer in which no TMA was reintroduced during the active layer growth. Although the minimum concentration is somewhat lower than in the uninterrupted growth, an aluminum "spike" is observed at the beginning of the layer. We can explain this observation as shown in Fig. 5. The TMG and TMA, after being turned off together, follow their own decay transients. Since TMG does not adsorb to graphite[6], its transient is much faster, thus causing a spike in the fraction of vapor-phase TMA and therefore, in the Al concentration of the solid.

In addition to their ability to act as a source and sink of TMA during $Al_xGa_{1-x}As$ growth, there are other effects of graphite baffles. In their earlier work, Kisker et al. proposed that the oxygen gettering effects which they observed
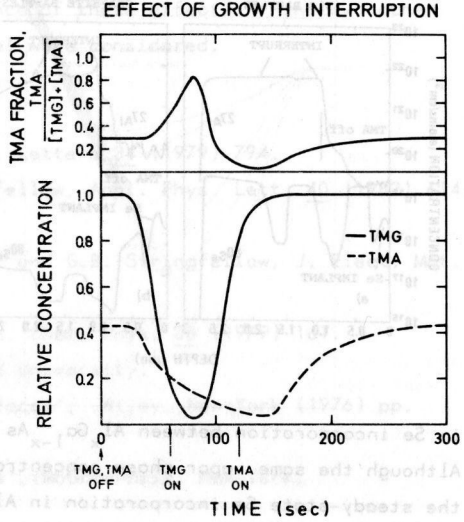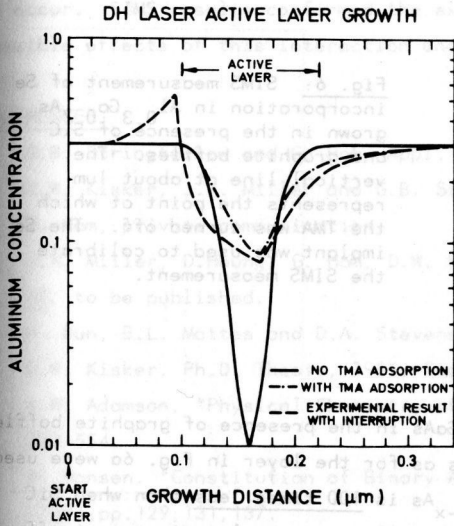
DH LASER ACTIVE LAYER GROWTH

EFFECT OF GROWTH INTERRUPTION

Fig. 4: Effect of adsorption on DH laser active layer. (——) calculated profile with no TMA adsorption; (—•—) calculated profile assuming TMA adsorption occurs; (———) SIMS measurement when growth interruption is used.

Fig. 5: Effect of growth interruption on active layer growth of DH laser.

were due to oxygen species reacting with pre-adsorbed TMA on the surface of graphite baffles[2]. Our work confirms the adsorption of TMA, its approximate surface concentration, and the lack of adsorption to quartz which explains the absence of an oxygen gettering effect with quartz baffles. The lack of oxygen gettering by SiC baffles[2] is probably due to the same effect, since like quartz, it is expected to be considerably more inert than graphite.

Another effect which can be explained by our TMA-adsorption model is the modified incorporation of selenium[4] when it is used as an n-type dopant during OMVPE. Because of the chemical similarity of the group VI elements Se and S and their compounds to the compounds of oxygen, we might expect a gettering effect similar to that for oxygen to occur when these atoms are used as dopants. (Note for example that aluminum forms stable compounds with Se and S as well as with oxygen[8].) In Fig. 6, we present the results of SIMS measurements on two layers grown to investigate this effect. After two cycles of H_2Se pulses with growth interruptions, the TMA was turned off and GaAs was grown. We make two observations about the layer shown in 6a, grown with SiC baffles: i) the steady-state Se concentration is the same in GaAs as in $Al_xGa_{1-x}As$, and ii) there is no evidence of any aluminum spikes resulting from the growth interruptions.

In contrast to the results for SiC baffles, the results shown in Fig. 6b, for a layer grown with graphite baffles clearly show evidence of the TMA-graphite-H_2Se interaction. First, the Al concentration spikes at the growth interruptions are present, as described above. Of greater interest however, is the large difference
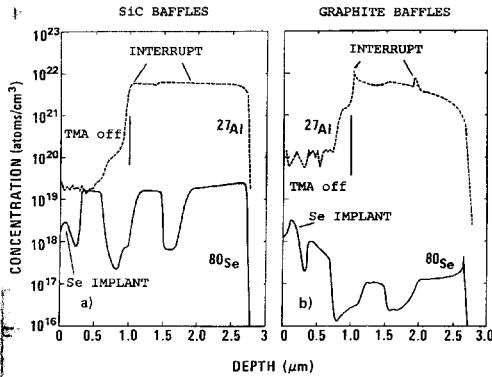
Fig. 6: SIMS measurement of Se incorporation in $Al_{0.3}Ga_{0.7}As$ grown in the presence of SiC and graphite baffles. The vertical line at about 1um represents the point at which the TMA was turned off. The Se implant was used to calibrate the SIMS measurement.

in Se incorporation between $Al_xGa_{1-x}As$ and GaAs in the presence of graphite baffles. Although the same vapor phase concentrations as for the layer in Fig. 6a were used, the steady-state Se incorporation in $Al_xGa_{1-x}As$ is <u>100 times less</u> than when SiC baffles are used! Further, though there is clearly an incomplete transient effect in the GaAs layer, the Se incorporation in GaAs is at least 10 times higher than in $Al_xGa_{1-x}As$. We also note that even when the H_2Se is turned off, the Se concentration does not reach its lowest value until the TMA is also turned off. These results indicate that although the H_2Se is gettered by the baffles, it must somehow be re-evolved during these periods.

    In addition to the results reported in this work, it is possible to speculate that other effects due to the TMA-graphite interaction should also be observed. One such possible effect would be a gettering effect for sulfur-containing compounds like those observed for oxygen- and selenium-containing compounds. To the best of our knowledge, such a result has not yet been reported. Similarly, although reports of strong variation of growth characteristics with temperature have not been made, because of the large energy of adsorption, such effects should be expected, and may result in run-to-run or reactor-to-reactor variability. Finally, as other OM compounds are used for sources of metallic components in semiconductor materials, either as a major component of a compound semiconductor, or as a dopant, it may be possible for other species to play a gettering role similar to that of TMA in the presence of graphite.

V. CONCLUSIONS: In this work, we have used a mass spectrometer with a molecular beam sampling apparatus to study the interaction of TMA with graphite as a function of temperature and graphite area. A value for the energy of adsorption of 15.7kcal/mole was found. The resulting strong adsorption of TMA onto graphite baffles provides the basis for a model which explains the oxygen gettering, selenium gettering, aluminum concentration spikes and long transient times for aluminum concentration changes observed during OMVPE. The baffles can thus act as not only a

source of TMA during transient processes, but as a site for the gettering reactions to occur. SIMS results confirmed the existence of these effects. Finally, other possible effects of this interaction and model were considered.

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