CHARACTERIZATION OF A SOLID-SOURCE DELIVERY SYSTEM FOR METAL ORGANIC CHEMICAL VAPOR DEPOSITION BY *IN-SITU* LASER REFLECTANCE

C. DUBOURDIEU*, G.Y. KIM, J.D. MEYER, B. GALLOIS
Stevens Institute of Technology, Department of Materials Science and Engineering, Hoboken NJ 07030
*Present address : Laboratoire des Matériaux et du Génie Physique, UMR CNRS 5628, ENSPG BP46, 38402 St Martin d'Hères, France

ABSTRACT

Specular laser reflectance (He-Ne laser) has been used to monitor *in-situ* and in real time the growth rate and the index of refraction of oxide films during chemical vapor deposition. This technique has been implemented on an inverted vertical stagnation-flow reactor equipped with a solid-source delivery system. Yttria deposited on silicon has been chosen as a starting material to characterize the reactor and the precursor delivery system capabilities. The experimental reflectance curves have been fitted to a simple three-layer (gas/film/substrate) model allowing the determination of the growth rate and of the refractive index. The growth rate has been studied as a function of various key processing parameters: the source feeding rate, the powder packing density, the oxygen partial pressure and the total pressure. The change in reflectivity has also been recorded during pulsed-delivery growth. Nanometer-scale resolution is obtained which demonstrates that this method can be extended to the study of multilayer oxide structures.

INTRODUCTION

A major drawback in the development of CVD growth systems and new materials is the multiplicity of operating parameters that need to be explored to optimize deposition conditions. This requires time consuming series of runs combined with *ex situ* characterizations. Specular laser reflectance is a flexible method to monitor *in situ* the thickness and index of refraction of a growing film in real time. It has been successfully employed to monitor the growth of III-V [1-4] and II-VI [5] compounds.

Laser reflectance is of particular interest in the case of metal organic chemical vapor deposition (MOCVD) of oxide films to evaluate quickly and in a cost-effective way new reactor geometries or novel precursor delivery schemes. Deposition of oxide materials require the use of organic precursors since they offer a higher volatility than halides compounds at temperatures of 100°C - 300°C. However, these organic precursors, mostly β-diketonates, suffer of poor thermal stability when heated at high temperature for a long period. To overcome this problem, new precursor delivery schemes have been developed during the past years, including the solid-source system designed by Hiskes *et al.* [6]. They have proven the versatility of this source layout in depositing various types of oxide films.

In this paper, we report on the implementation of the laser reflectance technique to monitor the growth of oxide thin films in a MOCVD reactor equipped with a solid-source delivery system. The laser reflectance has been used to evaluate the particular precursor delivery scheme and the reactor geometry. A major advantage of this technique is that information on film growth can be obtained

as the operating parameters are varied over large ranges within a single run. The measurements have been carried out in the case of yttria films grown on silicon substrates.

EXPERIMENT

A sketch of the reactor chamber and laser experiment is shown in figure 1. A linearly polarized He-Ne laser (λ = 632.8 nm) is used as the source light. The beam impinges onto the sample surface with an incidence angle close to the Brewster's angle of silicon and passes through a laser line filter and a beam splitter after reflection on the film surface. The s and p components are detected by two Si photodiodes and the currents are processed by two optical power meters. The experiment is interfaced to a PC *via* an analog-to-digital card. Data acquisition is conducted in real time by means of LabVIEW software. The acquisition time, after averaging the data, is 500 ms. The laser set-up is coupled to the reactor *via* two BK7 glass windows. The reactor is an inverted vertical stagnation-flow reactor. The solid-source delivery system comprises a stainless steel tube where the precursor powder is packed. The vaporizer consists of a micro-heater placed next to a water-cooled jacket in order to create a sharp temperature gradient. The tube is moved forward in the vaporizer using a variable-speed stepping motor. Argon is used as the carrier gas. This solid source arrangement ensures that the precursors is kept at a low temperature until it reaches the hot zone where flash vaporization occurs. This gives a better reproducibility compared to bubblers sources especially for high growth rate depositions.

To characterize this precursor delivery scheme yttria deposited on silicon substrates has been chosen as a starting material. $Y(tmhd)_3$ was used as the precursor. The effects of the feeding rate (determined by the motor speed) and of the powder packing density (mass of powder per unit length) have been studied over few deposition runs. These parameters determine the amount of precursor carried to the reactor chamber. A constant argon flow of 200 sccm was used. The typical deposition conditions are listed in table I.

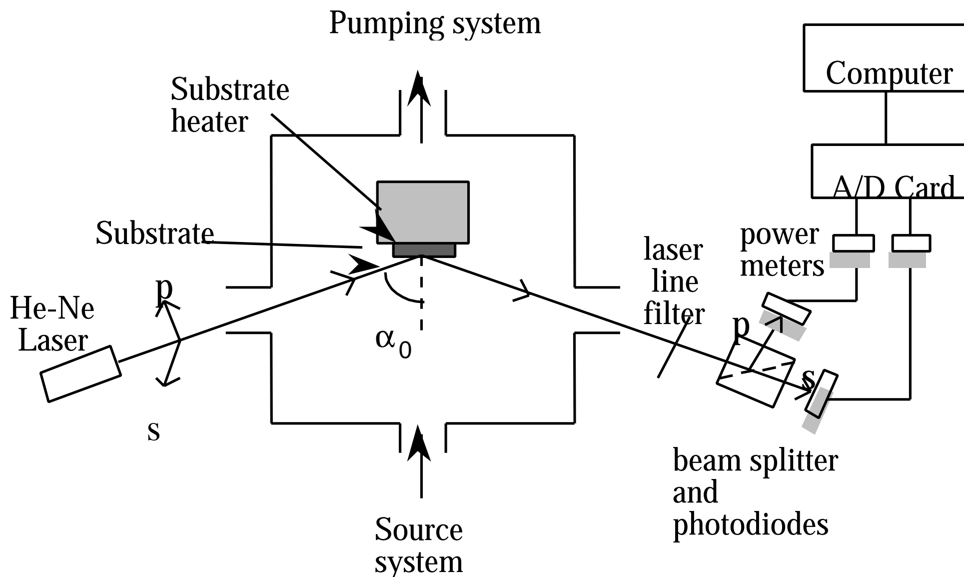

Figure 1: Sketch of the CVD reactor chamber and of the laser experiment.

Table I: Deposition conditions for yttria film growth

Parameter	Value
Substrate temperature	510 °C
Total pressure	2 - 10 Torr
Oxygen partial pressure	0.5 - 3.5 Torr
Argon flow rate	200 sccm
Micro-heater temperature	220 °C
Source feeding rate	0.0056 - 0.25 cm/mn

RESULTS

Calculation of the s and p reflectivities as a function of the film thickness for a three-layer system (air/film/substrate) using Fresnel's equations show oscillations with a period depending upon the angle of incidence α_0 and the dielectric function of the film. For a non-absorbing material of refractive index n_f, the period is given by:

$$\Delta D = \frac{\lambda}{2\sqrt{n_f^2 - \sin^2 \alpha_0}} \quad (1)$$

Typical experimental curves shown in figure 2 exhibit periodic oscillations over the run. At an incidence angle close to 75° the phase shift between the s and p components is π. An additional phase shift is observed, however, which might arise from birefringence in the two glass windows. Birefringence can be induced by strains due to pressure and temperature differences between the reactor chamber and the ambient atmosphere. From a comparison of the experimental to the calculated curves the growth rate and the index of refraction could be independently extracted. For a quick calculation of the growth rate the formula (1) has been used with a refractive index of 1.70 (yttria is transparent at the wavelength of 632.8 nm [7] so that the extinction coefficient k has been equaled to zero). Using this method the growth rate has been monitored under different operating conditions. Details about the yttria film properties will be reported elsewhere.

The importance of an uniform powder packing is shown in figure 3. The non-uniform growth rate is indicated by the numerous changes in the slope of the reflectance curve over just one period. Uniform powder packing leads to an uniform growth over a run as shown in figure 2. The optimum powder packing density was found to be in the range 0.10 g/cm - 0.15 g/cm. For the subsequent experiments a powder density of 0.15 g/cm was used. The change in growth rate when the feeding rate is varied is illustrated in figure 4. The s curve is shown together with the fitted curve. The growth rate calculated from the reflectance data is plotted in figure 5 as a function of the feeding rate. A linear relationship is observed. The growth rate can be therefore precisely controlled by

adjusting the precursor feeding rate. It can be varied by a factor of 40 in the range ~ 0.4 Å/s - ~16 Å/s.

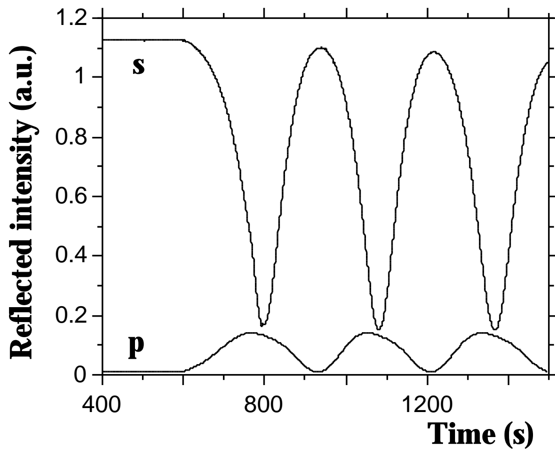

Figure 2: s and p reflectance curves during yttria growth.

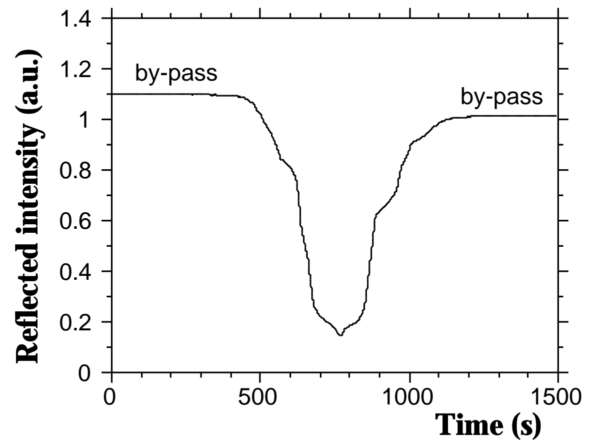

Figure 3: s reflectance curve showing the effect of a non uniform powder packing on the growth.

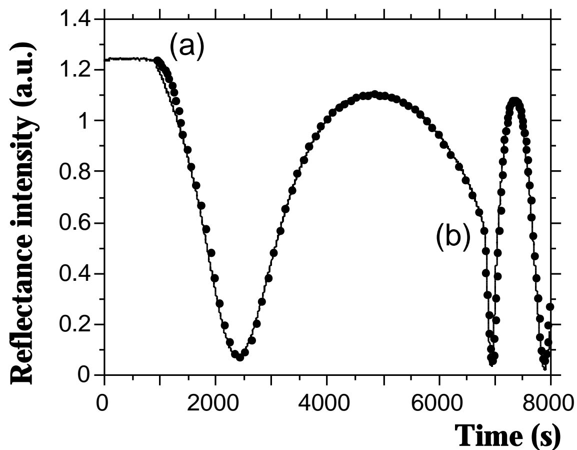

Figure 4: s reflectance curve while the source feeding rate is varied (a : 0.0056 cm/mn - b : 0.1 cm/mn). The straight line corresponds to the experimental curve, the dark points are for the fit.

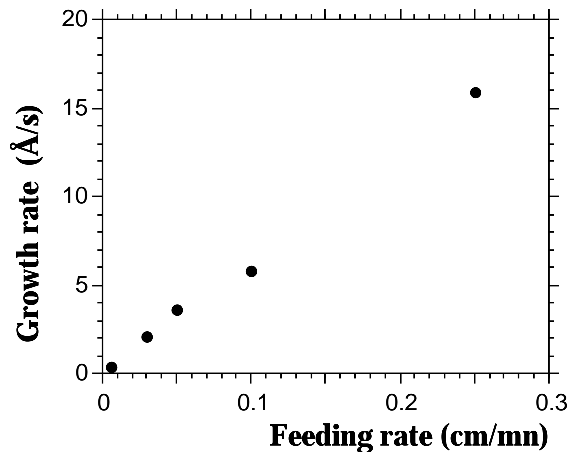

Figure 5: Growth rate calculated from the reflectance curves as a function of the source feeding rate (Ptotal = 3 Torr).

The effect of total pressure was also investigated. The total pressure was varied between 2 and 10 Torr with a fixed substrate temperature (510 ºC), fixed argon and oxygen flow (200 sccm each) and fixed source motor speed (0.1 cm/mn). A constant growth rate is obtained over the studied range within the experimental error. The total pressure has therefore not a significant impact in this range. In figure 7 is shown the effect of the oxygen partial pressure that was varied in the range 0.5 - 3.5 Torr by changing the oxygen flow rate. The growth rate increases with increasing oxygen partial pressure. A similar effect has been observed for $YBa_2Cu_3O_{7-x}$[8]. From a comparison of the amount

of precursor evaporated and the actual film composition, it was suggested that the yttrium precursor has a higher decomposition yield on the substrate's surface when the oxygen activity increases [9]. Moreover, the oxygen partial pressure can also affect the species mobility on the substrate's surface.

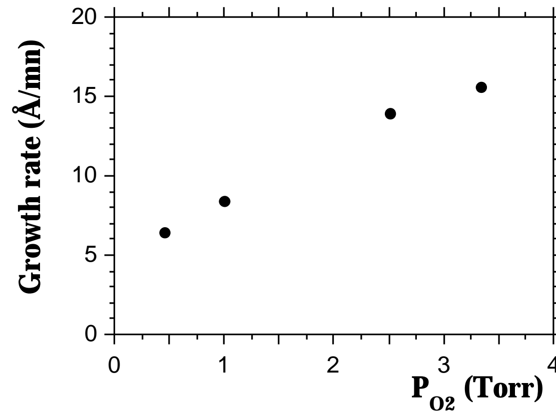

Figure 7: Growth rate calculated from the reflectance curves as a function of the oxygen partial pressure (Ptotal = 5 Torr).

From these experiments it was demonstrated that key parameters of the process can be quickly evaluated. The thickness of a simple oxide like yttria is measured without any need of *ex situ* measurements. Since most devices often involve more than one oxide, it is desirable to have the capability to monitor the growth of multilayers. This includes being able to determine the thickness of each layer at a nanometer scale and possibly to characterize the quality of the interfaces. The use of the laser reflectance technique for that purpose was demonstrated for amorphous silicon/silicon nitride superlattices [10] grown by conventional CVD. Using our solid source MOCVD system, the reflectance curves have been recorded during pulsed delivery growth. The vaporized precursor was sequentially directed to the by-pass line (for 5 s) and to the reactor chamber (for 5 s). As shown in figure 8, both s and p curves exhibit simultaneously plateaus every 5 s on the reflectance curve envelope. Each of the observed fine structure corresponds to a thickness of about 1 nm. This result demonstrates clearly that multilayer growth of interlayers can be monitored by this technique on a nanometer scale.

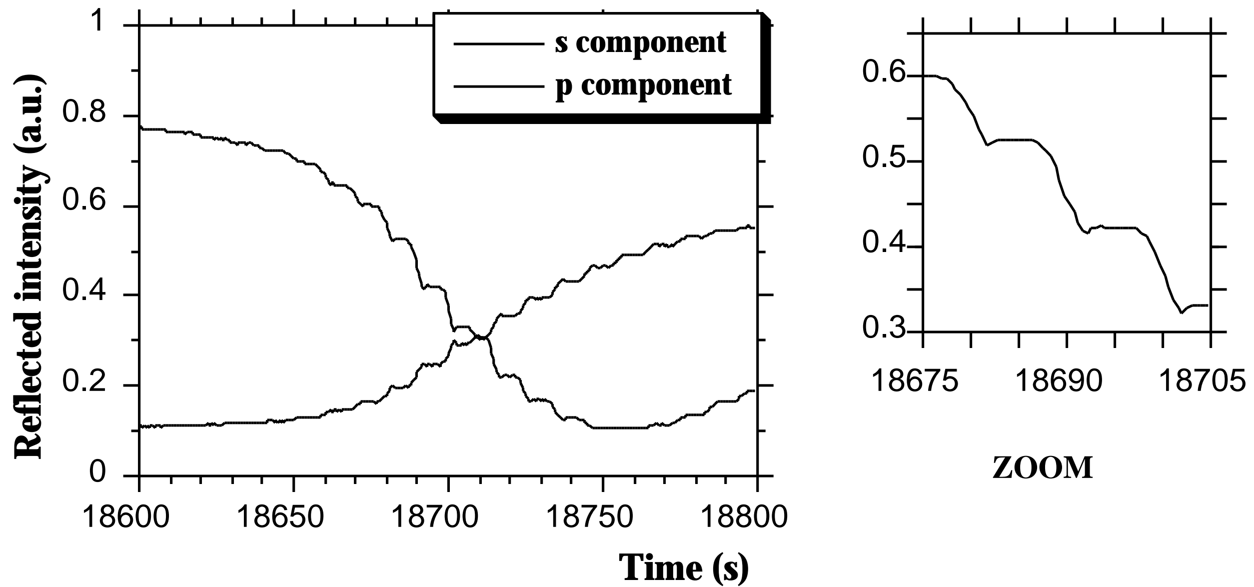

Figure 8: s and p reflectance curves during pulsed delivery growth. The zoom insert shows the fine structure of the p curve.

A finer structure (shoulders) also appear on the reflectance curves at the transition between growth and plateau as shown in the zoom of figure 8. These features could be related to the supply of precursor on the substrate's surface and to growth mechanisms.

CONCLUSIONS

The solid-source precursor delivery system used for metal-organic chemical vapor deposition of oxide films has been characterized by specular laser reflectance. It is shown that uniform growth can be achieved and that the growth rate can be controlled by adjusting the source feeding rate. It is also demonstrated that this technique can be used to monitor the growth of transparent oxide multilayers. The advantage of this method is that it is easily implemented whatever the size of the chamber. It is of low cost making it a very attractive tool to assess new precursor delivery schemes, characterize new reactor configurations and cut down the development time of new materials.

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