Development of a fluorescence based flux sensor for thin film growth and nanoparticle deposition

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An optical flux sensor, based on the fluorescence properties of materials and nanoparticles, has been developed to control the deposition rate in thin film deposition systems. Using a simple diode laser and a photomultiplier tube with a light filter, we report the detection of Gallium atoms and CdSe-ZnS quantum dots. This setup has a high sensitivity and reproducibility.

I. INTRODUCTION

Molecular beam epitaxy (MBE) is a widely used technique for preparing thin films. It is the standard for synthesis of highest quality coherent epitaxial films and heterostructures [1]. Since the element beam flux determines the growth rate for these films, it is important to measure this flux precisely [2]. Beam fluxes can be measured *in situ* by different techniques such as quadrupole mass spectroscopy (QMS), quartz crystal microbalance (QCM), electron impact emission spectroscopy (EIES), atomic absorption (AAS) and beam flux monitor (BFM, Bayard-Albert type). However, these techniques have their disadvantages. BFM is limited because of the finite lifetime of the filament. A QCM also has a finite crystal lifetime coupled with errors on the acoustic impedance of the already deposited material. To avoid these problems, optical techniques have been developed [3] using the fact that they require no need to replace filaments. Atomic absorption spectroscopy-based flux-monitoring tools usable during MBE growth have been demonstrated [4–6]. The main limitation to these direct absorption measurements comes from their rather low sensitivity, because typical experiments involve detecting a small loss of a large transmitted photon flux. A fluorescence method measures only the signal on top of a small background since the fluorescence signal comes only from the desired atoms. Nanoparticles (NPs) deposition systems bring new challenges. One of these challenges is the detection of the flux of NP directed at the substrate. When a NP vapor deposition technique (NVD) [7] is used, flow meters are capable of measuring the liquid flux; however, these flow meters have to be calibrated for every solvent used, thus limiting their versatility. Furthermore, it is not a direct measurement of the NP flux. Alternatively, the fluorescent signal of nanoparticles can be used to obtain a very fine control of the deposition rate. One of these ideas, proposed already some time ago, is to use a laser induced fluorescence intensity [8–10]. In this paper, flux measurements are demonstrated on two different

test systems. Firstly, on an atomic Ga flux and secondly on CdSe-ZnS quantum dots (QDs). We show that the technique is inherently linear with the flux, requires no equipment inside the vacuum system, and can be used during the growth process. This technique has the advantage that it can be used for all elements, molecules and compounds which have a fluorescence signal.

II. EQUIPMENT

A. Flux sensor device

A flux detector system, which includes a diode laser, a photomultiplier (PM) detector (Thorlabs PMM02) and a high-accuracy voltage meter (Keithley model 2001), was fabricated. The right part of Figure 2 shows the experimental arrangement. To ensure a low background signal level, a long tube is mounted from the PM flange to the flux area. This allows blocking of the background light inside the chamber. The number of optical components on the inside of the vacuum system was held as low as possible to avoid any coating problems. The gain voltage used was 0.95 V with the diaphragm aperture (Thorlabs SM2D25) fully open. A Thorlabs NF405-13 filter was used to block the PM from the incident laser light (403 nm). To block the PM from red/ir wavelengths, which might come from the hot cell, a Thorlabs FES0500 filter was used. Finally, a Thorlabs NE20A-A neutral density filter was used to decrease the total signal level to an acceptable level for the PM. The PM output signal was measured by a Eurotherm controller, which was also used to control the gain voltage of the PM. By doing this the size of the flux sensor system stayed compact. The detector and laser mounting were made in two different ways. In the first version, both were mounted side by side in a way that stray light from the chamber is minimized (see left part Figure 1). In the second version, both were mounted perpendicular to each other (see right part Figure 1). The latter gave the possibility to mea-

Figure 1. (Left) First version of the test system for atomic Ga flux measurements with side by side mounting of the detector and laser. (Right) Second version with perpendicular mounting of detector and laser.

sure the flux with alternative flux sensors. The second setup used a gain voltage of 0.65 V and the diaphragm aperture was fully open. Only two filters were used in this setup: a Thorlabs NF405-13 filter and a Semrock Brightline FF01-425/26-25 filter, which is a single-band bandpass filter at the fluorescence wavelength of Ga (417 nm).

B. Atomic Ga flux measurements

DCA Instruments specially designed and manufactured an ultra high vacuum (UHV) system to test the fluorescence flux sensor. A standard DCA dual filament effusion cell was used for Ga evaporation in an MBE system. The effusion cell was mounted into a water cooled stainless steel tube at 300 mm distance from the cell. The distance is selected to be the same as in DCA P600 MBE systems for III-IV epitaxy. A movable beam flux monitor (BFM, DCA) based on a Bayard-Alpert type ionization gauge, was used as an alternative flux monitor. Ga excitation was performed by a diode laser at 403 nm (Toptica Photonics iBeam smart 405 tuned to 403 nm). The fluorescence wavelength of Ga is 417 nm.

C. NPs flux measurements

The CVD system used for the deposition of the NP thin films was also designed and manufactured by DCA Instruments. The experimental arrangement of the process chamber can be seen in the left part of Figure 2. A detailed description of the complete CVD system as well as the first depositions with NPs is reported in a paper by Vervaele *et al.* [7]. A Direct Liquid Injection (DLI) vaporizer (Vapbox 1500, Kemstream) was mounted on top of the CVD process chamber allowing to perform DLI-CVD processes. The DLI vaporizer allows a controlled pulsed injection and vaporization of NP solution. The average flow rate of the NP solution and the carrier gas can be adjusted by changing the injection parameters (injection frequency, injectors opening time, solution flow setpoints and carrier gas flow setpoints). Heating of the 2 inch substrate is possible up to 1000 °C with rotation speeds up to 60 RPM. The distance between the substrate and the NP injector outlet can be varied between 157 mm and 257 mm. The QDs were excited with a 515 nm laser (Thorlabs iBeam smart 515). Since the maximum emission wavelength (600 nm) of the QDs used in the following experiments was further away from the laser excitation wavelength (515 nm) and no heat was produced by any evaporation cell, the need for filters was diminished and we only used a Semrock FF01-609/57-25 to block the background signal.

Figure 2. Experimental arrangement of the CVD system. (Left) The process chamber with illustration of the vapor flux and substrate. The NP injector, viewport and downstream control are also indicated. (Right) The NP flux sensor with the diode laser, excitation laser beam and photomultiplier detector.

III. EXPERIMENTAL METHODS

In this work, two experiments are shown. For the first experiment atomic Ga evaporating from a high temperature effusion cell was used to validate the flux sensor. The cell temperature was varied between 800 °C and 1200 °C, which is a typical temperature range for Ga evaporation in a GaAs MBE system. The background pressure in the chamber was between 10^{-8} - 10^{-9} Pa during the experiment.

In the second series of experiments, CdSe-ZnS QDs, from Sigma-Aldrich having a diameter of about 5 nm, were used. These QDs have their fluorescence emission peak at 600 nm. The QDs were loaded in the DLI-CVD system, and were deposited on a 2 inch silicium substrate. The following parameters were used: anhydrous nitrogen was used as gas carrier, the carrier gas injection frequency was 3 Hz, the nanoparticle solution injection frequency

was 1.5 Hz, the carrier gas pressure was 350 kPa and the solution pressure was 250 kPa. The vaporization temperature was 115 °C and the substrate temperature 150 °C. Flow rate and time were the only variables in this experiment. A concentration of 30 mg QDs / 300 ml cyclohexane (NP solution) was used.

IV. EXPERIMENTAL RESULTS

A. Ga flux

The fluorescence signal as a function of cell temperature was compared to the BFM flux reading. The cell temperature was increased from 800 to 1200 °C with discrete steps. After every temperature increase the cell temperature was first stabilized; then the fluorescence signal was recorded for 1 min and the average value of

the fluorescence signal was taken. The same procedure was used for the BFM reading. The results of both flux measurement methods were consistent, as can be seen in Figure 3. A small deviation can be seen at low temperature. For low temperature the BFM is still measuring the background pressure while the background of the fluorescence signal has been subtracted. The image shows that we can use this method to detect gallium pressures from $5.6 \cdot 10^{-7}$ Pa up to at least $1.6 \cdot 10^{-5}$ Pa, which are MBE relevant pressures. The upper limit of detection will be much higher since this is an optical fluorescence technique. Pearsall *et al.* [9] did measurements of Ga species in a partial pressure range up to 57 kPa, which is appropriate for CVD processes.

Figure 3. Results from atomic Ga flux measurements compared with the ion gauge beam flux monitor. The background of the fluorescence signal has been subtracted.

The repeatability of the signal was measured by measuring the fluorescence signal while changing the cell temperature between 1180 and 2000 °C 3 times (Figure 4). The average values of the 1200 °C runs were within 0.5 % of each other. For this configuration, the sensor has a sensitivity of 0.05 V/ 20 °C.

These results indicate a good reproducibility of the results and the variations lay well within the error margins of the temperature control of the effusion cell. The fluctuations can be explained by small variations in temperature, which have a large influence on the flux.

Figure 4. Signal repeatability at different Ga source temperatures as a function of time.

The long term stability of the fluorescence signal was recorded over a 13 h period. The fluorescence intensity is very stable, it does not deviate more than 2 % from the average fluorescence intensity over 13 hours, as can be seen from Figure 5. Small fluctuations, which can be seen in the signal, may be caused by the laser diode temperature fluctuation as well as small changes in Ga flux. The diode temperature is kept constant with an internal Peltier element, but already a small change in the diode temperature might cause wavelength shifting, which affects the overall output signal.

Figure 5. Signal of Ga flux at 1100 °C for over 13 h of continuous monitoring.

Although the results are now already comparable with traditional flux measurement methods such as QCM and BFM, it must be stated that the signal-to-noise ratio and the stability of the signal can still be greatly improved by chopping the laser beam and by using a lock-in amplifier. The fluorescence based flux measurement can also be used in other deposition techniques. Special care needs to be taken in high pressure system since there is no guarantee that the Ga does not start clustering. During evaporation, nanodroplets might be formed. This process is governed by thermodynamic conditions (pressure, temperature) and the concentration of Ga during the nucleation time of the droplets[11].

B. Quantum dots

The results of the QD flux signal levels are shown in Figure 6. The flow rate was varied from 0.05 g/min to 1.4 g/min. The injector was operated during 1-2 minutes and was then stopped again. An increase in signal could be seen with increasing flow rate. These experiments show that it is possible to measure the deposition flow of QDs in real-time thanks to their fluorescence properties.

Figure 6. Voltage signal obtained from the flux measurement with the fluorescence sensor as a function of time. The flow of QDs was manually changed several times to observe the response of the device. Each square reflects a moment of time in which the flow was turned on and its width indicates the duration. The number inside the square indicates the flow in g/min. The background has been subtracted in order to have a good comparison between the flow rates.

This result shows that a one-to-one relationship can be found between the flux of the QDs and their fluorescence signal. A fitting of the average fluorescence intensity versus flow was done to be able to interpolate the flux for different flow values. The average intensity was calculated by first normalizing the intensity to the laser power and then by averaging the intensity over the duration that the pulse was on. The average background taken at one minute before a flow pulse started and at one minute after the flow pulse was stopped, was subtracted from the fluorescence intensity. This yielded results as shown in Figure 7 suggesting two different trends which were each fitted by a linear function. We obtained a detection limit from the first fit. The minimum flow necessary to obtain a signal above the noise level was 0.26 g/min. A change in slope was seen from $7.5 \cdot 10^{-3} \pm 0.3 \cdot 10^{-3}$ to 0.036 ± 0.002 when increasing the flow above 1 g/min. Aggregation and/or agglomeration effects could explain this, which cause clusters of QDs to be present in the evaporated QD solution. During evaporation of the QD solution, nanodroplets might be formed. These nanodroplets can then induce agglomeration and/or aggregation of the nanoparticles. This process is governed by thermodynamic conditions (pressure, temperature) and the concentration during the nucleation time of the droplets [11]. When we adapt the flow rate, the pressure and concentration of QDs inside the evaporation chamber changes. In that case a larger slope can be explained by a focusing effect of the QDs. Since clusters are more massive than single nanoparticles, the beam of nanoparticles will diverge less and hence have a higher flux density at the position of the laser. As such we expect to go from one regime to another at a flow of 1 g/min, where we get more aggregation/agglomeration at the higher flow rates. In addition, results on 2 nm gold NPs have already shown that aggregation of gold NPs takes place when the flow speed is increased beyond 0.5 g/min [7]. A similar behav-

ior is probably taking place with the QDs in this study, but at a different flow speed due to the differences in NP sizes and surface layer. The clustering can also be used to explain the increase in noise at higher flux rates, since we probably have a few very large clusters that give a very high signal. These large clusters will not be the whole time in the laser beam, creating large fluctuations in the intensity. The noise at low speeds can be explained by the pulsed nature of the system, which gives some variation in the measured intensity.

Figure 7. Averaged fluorescence signal versus different flow rates and the two fitted lines in the two areas.

Since the DLI is a pulsed injection system, the shape of pulse itself can be seen via the fluorescence signal of the QDs. The data collection rate on the sensor is about 10 datapoints per second. The graph in Figure 8 has been obtained by measuring the fluorescence intensity when a 1 Hz injection speed was used. The graph clearly shows the 1 Hz frequency and the sinusoidal behavior of the injected flux of QDs. This shows some pulse to pulse variation.

Figure 8. The fluorescence intensity at a 1 Hz injection speed fitted with a sinusoidal function.

V. CONCLUSION

We have developed and tested a fluorescence based flux meter for monitoring a molecular beam of Ga or for the detection of fluorescent nanoparticles. We confirmed that

there was a strong Ga source temperature dependent signal with a good repeatability and sensitivity as a function of temperature. In general, it can be stated that fluorescence based flux measurements can be used in MBE, opening a lot of new sensor opportunities which have not been available earlier.

In order to test the flux detector for NP in the vapor phase, CdSe-ZnS quantum dots injected from a DLI - CVD reactor were analyzed. This flux detector can be used as a complementary technique to the liquid flow meters of the CVD system for measuring the flow rates of NPs being deposited onto a substrate. This will increase the range of flows that can be used in these applications, since the liquid flow meters currently used are limited to measuring the flux up to 3 g/min.

While fluorescence based flux monitoring is not the only way to obtain information on deposition rates, it is

one of the few simple techniques that can give real-time information on the deposition rate. Furthermore, this technique is non-invasive to the growth chamber and only requires optical windows.

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