

## How to avoid concentration unsteadiness with a CVD precursor delivery system employing bubbler?

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**Abstract.** An approach of great certainty is suggested as to avoid concentration unsteadiness with a CVD delivery system employing bubbler. Assuming that the carrier gas has to be saturated of precursor vapour during the entire CVD experiment a set of equations has been selected from the literature for calculating the height of liquid layer in the bubbler which is necessary to this aim. The selection is made on the prerequisites that gas bubbles are spherical, diffusion of precursor vapour in them is molecular and it takes place during their rising only, which has a velocity equal to the terminal bubble velocity of rising. The errors at levels lower than the one for saturation are discussed. Heights of  $\text{Al}(\text{CH}_3)_3$  calculated using the approach are compared to those at which the bubbler controlling LED indicator of Dow Electronic Materials lights green, amber or red.

### 1. Introduction

The precursor delivery system is an important integral part of any CVD set-up. Very often this system utilizes bubbler wherethrough the carrier gas is passing and uptakes precursor vapour. In the case of multicomponent coating each component is usually delivered from a separate bubbler. The constant precursor concentration in the gas mixture entering the CVD reactor is unavoidable condition for correct research and production of high quality, therefore the precursor concentration in the carrier gas exiting the bubbler should be kept constant. The gas saturation has been approved as a basic principle for this constancy [1]. This requires maintaining a sufficiently high level of the liquid precursor in the bubbler. For this purpose, methods for control of the level [2] or to keep it constant [3] have been developed. The system with a self-metering reservoir is very complicated and in many cases – inapplicable [3]. Some companies offer various precursors in bubblers with visual liquid multi-level indicator for trademark (TM) vaporization delivery system and guarantee maximum source consumption [4]. The number of new liquid precursors however is increasing. The cost of the TM delivery systems and bubblers are very high and some researchers have to use in house made CVD set-up and bubbler. In such cases it is necessary to predict the precursor level at which the carrier gas will exit the vessel fully saturated during the entire deposition process.

The aim of the present work is to propose an approach which will provide such prediction with high certainty. This approach can be used in many other cases where gas-vapour mixture with constant concentration has to be prepared by bubbling. Typical examples are preparation of such mixtures for research in adsorption and catalysis as well as humidifying of gases.



## 2. Theoretical analysis

The carrier gas in the bubbler is in contact with the precursor from the bubbles formation until their break-up on the liquid surface. At some conditions the breaking results in formation of small drops which may evaporate. Neglecting this vaporization and the mass transfer during the bubble formation and residence time in the foam layer is the first point of the approach.

The mass transfer from the liquid into the rising bubbles is a diffusion with a constant concentration at the interface,  $C_i$ , which is determined by the vapour pressure of the liquid at its temperature. Therefore the rate of mass transfer will depend on the diffusion resistance in the gas phase only. The latter depends on the bubble shape and hydrodynamic conditions in it. They are both influenced by the bubble size. The very small bubbles ( $d \ll 1$  mm) are spherical and the gas phase in them is immobile [5-7]. They behave like rigid spheres and the vapour penetrates in them by molecular diffusion. The differential equation for such unsteady-state diffusion with constant concentration at the interface has analytical solution valid when  $R \rightarrow 0$  [8]

$$\frac{C - C_1}{C_i - C_1} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-Dn^2 \pi^2 t / R^2\right) \quad (1)$$

According to the simplifications already made, the initial concentration,  $C_1$ , should be zero and the time of contact should be

$$t \geq H/w \quad (2)$$

In relation (2)  $H$  is the liquid height over the place of bubbling and  $w$  - the bubble velocity. The small spheres rise vertically and for them the sign of equality is applicable. The path of bigger bubbles is more complicated [5-7] but for them assuming the equality will increase the certainty of prediction. Accounting for these considerations Eq. (1) may be transformed:

$$\Delta = 1 - \frac{C}{C_i} = -2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-Dn^2 \pi^2 H / wR^2\right) \quad (3)$$

Equation (3) has been numerically solved up to the nearly complete sphere saturation, i.e. for  $C \in [0, C_i]$ , at the sphere centre, and the results obtained are tabulated [7]. They are given in table 1 together with some values obtained from figure 6.1 in [8].

**Table 1** Numerical results according to equation (3).

$Dt/R^2$	0	0.032	0.080	0.100	0.160	0.240	0.30	0.320	0.40	0.800
$\Delta$	1	0.9975	0.8276	0.7071	0.4087	0.1871	0.104	0.0850	0.040	0.0007

It can be seen that at  $(Dt/R^2) = 0.800$ , the concentration in the bubble centre will be  $C = 0.9993C_i$ .

At 0.4  $C$  will be 96% of  $C_i$ , but the average concentration will be much nearer to  $C_i$ . The exact results can be found from the next equation [8]:

$$\frac{M_t}{M_{\infty}} = \frac{C_{av}}{C_i} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-Dn^2 \pi^2 t / R^2\right), \quad (4)$$

or by means of table 2 [7].

**Table 2** Variation of dimensionless concentration,  $\Delta'$ , with  $Dt/R^2$ .

$Dt/R^2$	0	0.005	0.01	0.02	0.04	0.06	0.1	0.2	0.3	0.5	0.8
$\Delta'$	1	0.774	0.690	0.579	0.440	0.352	0.226	0.084	0.031	0.0043	0.0002

In table 2  $\Delta'$  is  $(C_i - C_{av}) / (C_i - C_1)$ . At  $C_1 = 0$  and  $Dt/R^2 = 0.8$ ,  $C_{av} = 0.9998C_i$ . If the value of 0.8 is agreed as a condition for saturation of the bubbles, the necessary height to this aim,  $H$ , can be found from the relation

$$H = \frac{0.8wR^2}{D} \quad (5)$$

In the particular case of substance A diffusion into the gas B, which takes place in the process of saturation, the diffusivity coefficient,  $D$ , can be found from the relation of Fuller et al. [9]

$$D_{AB} = \frac{10^{-3} T^{1.75} (1/m_A + 1/m_B)^{1/2}}{P \left[ (\sum \nu_A)^{1/3} + (\sum \nu_B)^{1/3} \right]^2} \quad (6)$$

or the relation of Maxwell/Gilliland [10]

$$D_{AB} = \frac{4.3 \times 10^{-3} T^{3/2} (1/m_A + 1/m_B)^{1/2}}{P \left[ (\sum \nu_A)^{1/3} + (\sum \nu_B)^{1/3} \right]^2} \quad (7)$$

Experimental data are also available for some binary mixtures [9,10].

The rising velocity of a bubble,  $w$ , depends on its volume. The increasing of the volume results in a change of the bubble shape from spherical through ellipsoidal to semispherical and flat [5-7]. For a given gas-liquid system the shape can be controlled by the diameter of the bubbler holes,  $d_0$ , and the gas flow rate,  $V_0$ . If the latter is smaller than a critical value,  $V_{0c}$

$$V_{0c} = \frac{\pi d^2}{6} w \quad (8)$$

and the liquid is wetting the bubbler material

$$d = \left( \frac{6d_0\sigma}{g(\rho_L - \rho_G)} \right)^{\frac{1}{3}} \quad (9)$$

Selecting  $d_0$  one can obtain spherical bubble for which eqs. (3), (4) and Tables 1, 2 are applicable. As a first iteration  $d \leq 1 \div 1.5$  mm is a required condition [5-7].

The chosen value of  $d$  allows the calculation of rising velocity,  $w$ . In the case of bubble however there is no well-established opinion which equation is the most correct [5-7]. The rigid sphere behaviour found in several investigations has been attributed to the presence of surface active agents in the liquids used [5] and the Rybczynski-Hadamard relation for circulating drop adopted for bubble has been recommended at  $Re < 1$  ( $gR^3/3\nu^2 < 1$ ) [5].

$$w = \frac{1}{3} \frac{(\rho_L - \rho_G) g R^2}{\mu} \quad (10)$$

The latter predicts higher velocity than Stokes relation for rigid sphere

$$w = \frac{2}{9} \frac{(\rho_L - \rho_G) g R^2}{\mu} \quad (11)$$

and thus increases the certainty of saturation. Regarding eq. (8) however eq. (11) has to be used and lower value of  $V_{0c}$  will be obtained. If the carrier gas flow rate of this value will be insufficient for the CVD, the precursor temperature, number of bubbler holes or both can be increased as to deliver the required precursor quantity.

The requirement  $gR^3/3\nu^2 < 1$  together with eq. (9) results in very small bubbler holes corresponding to sintered materials. Cappillary tubes may produce bubble with diameter in order of

$10^{-3}$  m, which may deviate from spherical but the equations and tables already discussed can be also applied. This is justified by the smaller path of penetration as well as by the increased circulations or oblate-prolate oscillations of the bubble which create convective diffusion.

For bubbles of such dimensions the value of Reynolds number is usually above 400 and the following relation can be used for calculating the velocity [5]:

$$w = 6.603\sqrt{R} \quad (12)$$

It is important to note that eqs. (11) and (12) predict the terminal rising velocity after a short period of acceleration, therefore the real bubble residence time will be somewhat longer. The bubbles successively obtained are not exactly alike.

The diameter and velocity of the bubbles can be determined experimentally as well. Techniques to this aim have been well developed.

It should be pointed out that the concentration unsteadiness is not very sensitive to the exact calculation of liquid height in the bubbler. Data in Table 2 show that if value of 0.2 is chosen instead of 0.8 for calculating the height above which the liquid level should be maintained, the maximum change of the average precursor concentration will be of 8.4 % below the saturation. At 0.3 it will be 3.1 %.

### 3. Some illustrative numerical results

To evaluate the suggested approach we shall use the available information about DOW bubblers with liquid multi-level indicator [4]. LED lamps of three colors light when the level is: green – above 20 %, amber – between 20 % and 10 % and red – below 10 % of the initial precursor height respectively. For TM bubbler with height of 108 mm, diameter of 51 mm and liquid volume of 150 ml, the initial level is 80 mm and the levels at which the respective lamp will be lit-up are >16, 16-8 and <8 mm. For TM bubbler with precursor volume of 3000 ml, the respective dimensions are 254, 127 and 240 mm. The levels for the respective color are >48, 48-24 and <24 mm. In Table 3 the minimum levels required for saturation of nitrogen with  $\text{Al}(\text{CH}_3)_3$  (TMA) vapor, calculated from the respective equations are shown for two often used capillary diameters.

The TMA diffusivity coefficient is found from Eq. (7). The other characteristics are as follows: surface tension –  $0.0261 \text{ N m}^{-1}$ , viscosity –  $0.94 \times 10^{-3} \text{ Pa s}$  and density –  $750 \text{ kg m}^{-3}$ . All data are at temperature of  $28^\circ \text{C}$ .

The results of Table 3 seem very realistic. Experiments for a more precise evaluation of the approach will be aim of a future work.

**Table 3** Illustrative calculations for the levels of  $\text{Al}(\text{CH}_3)_3$  allowing comparison with DOW proposals.

No	capillary diameter, $d_0$ , mm	bubble diameter, $d$ , mm Eq. (9)	rising velocity, $w$ , $\text{m s}^{-1}$ Eq. (12)	Reynolds number Re	required level, H, mm Eq. (5)	level at deviation of 3% from saturation, mm
1	0.5	2.21	0.220	387	>23.6	8.8
2	1	2.79	0.246	547	>42	15.7

### 4. Conclusions

The theoretical analysis of the problem has shown that as to avoid a concentration unsteadiness the precursor level in a bubbler must be kept above a certain critical value during the entire deposition process. This value depends on many factors (diameter of the bubbler holes, precursor density, viscosity, surface tension and diffusivity in the carrier gas, bubble shape and dimensions, gas flow rate, temperature, etc.) which have to be accounted for with each particular case. An approach for

calculating this value is suggested. It reveals a moderate sensitivity of the unsteadiness from the changes of this level, but they should be considered regarding the precision of CVD experiments.

### Notations

$C$	current local precursor concentration ( $\text{kg m}^{-3}$ )
$C_1$	initial precursor concentration in bubble ( $\text{kg m}^{-3}$ )
$C_{av}$	mean current precursor concentration ( $\text{kg m}^{-3}$ )
$C_i$	concentration of saturation ( $\text{kg m}^{-3}$ )
$D$	diffusivity coefficient of the precursor vapour in the carrier gas ( $\text{m}^2 \text{s}^{-1}$ )
$d$	bubble diameter (m)
$d_0$	diameter of the bubbler holes (m)
$g$	Earth acceleration ( $\text{m}^2 \text{s}^{-1}$ )
$H$	height of liquid above the place of bubble formation (m)
$M_A$	molecular mass of the carrier gas ( $\text{kg mol}^{-1}$ )
$M_B$	molecular mass of the precursor ( $\text{kg mol}^{-1}$ )
$M_t$	precursor mass in the bubble at time $t$ (kg)
$M_\infty$	precursor mass in the bubble at saturation (kg)
$P$	pressure (atm)
$R$	radius of the bubble (m)
Re	Reynolds number, $\frac{wd\rho_L}{\mu}$ (-)
$T$	temperature (K)
$t$	residence time of the bubble in the bubbler liquid (s)
$V_{oc}$	critical carrier gas flow rate ( $\text{m}^3 \text{s}^{-1}$ )
$V_o$	carrier gas flow rate ( $\text{m}^3 \text{s}^{-1}$ )
$\nu$	kinematic viscosity ( $\text{m}^2 \text{s}^{-1}$ )
$w$	terminal rising velocity of the bubble ( $\text{m s}^{-1}$ )
$\mu$	precursor viscosity (Pa s)
$\rho_G$	carrier gas density ( $\text{kg m}^{-3}$ )
$\rho_L$	precursor density ( $\text{kg m}^{-3}$ )
$\sigma$	surface tension precursor/carrier gas ( $\text{N m}^{-1}$ )
$\nu_A$	molecular volume of the carrier gas
$\nu_B$	atomic volume of the precursor elements

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Chapter 8

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