Statistical study of the variable speed of an AACVD device implemented in the UTP

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Abstract. The spray assisted chemical vapor deposition (AACVD) technique is used to make thin film growth through the spraying of a precursor solution in the form of droplets, by means of a nozzle moving horizontally along the substrate. One of the most influential variables in the growth of the films is the speed with which the nozzle moves, since the deposition uniformity depends on this, which is directly related to the different physical properties of the coating. This paper briefly shows the electronic control built for the manipulation of this variable and a statistical study is presented that allowed to determine that the experimental speed presents oscillations less than 10% with respect to the programmed value. In addition, comparative transmittance spectra are shown where the reproducibility and repeatability of the coatings manufactured with the AACVD equipment built in the UTP is observed.

1. Introduction.

The technique of chemical vapor deposition assisted by aerosol (AACVD) is widely used due to its easy implementation and low cost of operation, both in universities and companies, for applications in the area of basic science and study of materials [1-4]. This technique consists in atomizing a precursor solution and with the help of a dragging gas at controlled temperature gas, it is transferred to the spout of a nozzle that moves horizontally at a constant speed, in order to deposit the solution along a substrate, leaving and form a thin film on its surface. The physical characteristics of the coating (structure, thickness, uniformity, etc.) depend on parameters such as: the temperature of the substrate, the dragging mass flow of the drag, the number of layers and the speed of displacement of the nozzle [5].

One of the most important variables during the deposit is the constant speed of displacement of the nozzle, due to its direct influence on the uniform distribution of the coating [6], since this can affect the optical, thermal, and magnetic properties, thickness, roughness, among others, which are the objective of study of this in research. This paper presents a brief description of the speed control implemented for the AACVD equipment that was built in the Research Group on Optical and Magneto-Optical Properties of New Materials (GIMM) of the Technological University of Pereira (UTP) in of Colombia. In order to determine the oscillation range between the programmed and the experimental speed, a statistical study was carried out showing the error, dispersion, variance, uncertainty, among other characteristics.
In addition, titanium oxide coatings were deposited on glass substrates at different speeds, transmittance spectra were analysed at different points of the coating in order to determine the uniformity of the films.

2. Implementation of the control and statistical study of the speed variable speed.

Figure 1, shows the components that make up the AACVD team which was made the statistical analysis

![Figure 1. Components AACVD equipment, (1) Heating plate, (2) nozzle, (3) stepper motor, (4) auger, (5) nebulizer, (6) flow regulator, (7) calefactor, (8) compressor, (9) calefactor control, (10) process control (speed, # layers, delay between layers, distance), (11) temperature control of the hot plate, (12) gas extraction cabinet](image)

2.1 Implementation of speed control

For the displacement assembly of the nozzle, a stepper motor was used (sensitivity of 0.9 degrees, 400 steps per turn and nominal torque of 4.2 kg cm⁻¹) joined together with a screw with a pitch of 1.500 mm per turn and supported at one end by a bearing; parallel to this is an aluminum rail on which rests a skate that moves bidirectionally driven by the auger. A mast is erected on the skate, where a Teflon-based support made out of Teflon is located, which serves as the base for the nozzle and where the precursor solution enters through a hose. For the control of this system an algorithm was implemented in multiplatform software Arduino, which allows to vary the engine’s rotations speed of rotation of the engine and through the mechanisms mentioned above, moves the nozzle at a speed in a range between (0.200 cm min⁻¹ - 1,000 cm min⁻¹). The operating principle of the control system is based on the input parameters, which are entered into the control system through an alphanumeric keyboard, these parameters are: speed, number of layers, delay between layers and distance deposit. After this, the control reads an ultrasonic sensor, and based on the value of the signal, makes the respective decisions according to the initial conditions given. An important parameter to achieve homogeneity in the tanks is the stability and accuracy of the speed of the nozzle, because if it does not move at the same speed along the horizontal axis there will be accumulations of material in areas where the speed changes, manifesting as resulting in areas of different thickness and texture (for the case of titanium oxide, lines of different color are observed in the substrate). If the nozzle speed changes between layers showing a low accuracy, the deposits with different thicknesses will be different obtained than expected, thus changing its optical and micro-structural properties.

2.2 Statistical study of the speed variable

It was determined experimentally that to obtain deposits with similar physical characteristics, variations in the speed should not exceed 10% of the programmed speed, and for this purpose a series of experimental tests were carried out to determine the speed error. Of the nozzle in the established range of use.
2.2.1 Accuracy test. For this test, five different speeds were taken, starting at the minimum speed and increasing in steps of 0.200 \text{ cm min}^{-1} until reaching the maximum speed, taking measuring 5 times each point in order to determine accuracy and precision in the displacement of the nozzle. The maximum distance travel that the nozzle travels can make is 11 cm, and displacement tests have been made up to the maximum allowed distance in order and to determine the homogeneity of the trajectory by measuring the time and distance for each route run was measured, and using the following mathematical relationship as it is shown in equation (1).

\[ V = \frac{D}{T} \]  

(1)

Where \( V \): is the speed of the nozzle, \( D \): Distance that travels and \( T \): Time that it takes to run the distance do that route at constant speed.

Table 1 summarizes the experimental data of the distance and time that the nozzle did used when moving with constant speed introduced by the operator in a range of 0.200 \text{ cm min}^{-1} to 1,000 \text{ cm min}^{-1} every 0.200 \text{ cm min}^{-1}.

**Table 1.** Time and distance data taken experimentally for each of the programmed speeds in the equipment.

| Theoretical speed \( V_r \) (cm min\(^{-1}\)) | Data 1 | Data 2 | Data 3 | Data 4 | Data 5 |
|---------------------------------------------|--------|--------|--------|--------|--------|
| Distance (cm) | Time (min) | Distance (cm) | Time (min) | Distance (cm) | Time (min) | Distance (cm) | Time (min) | Distance (cm) | Time (min) |
| 0.200 | 11.272 | 53.454 | 11.301 | 53.451 | 11.336 | 53.457 | 11.356 | 53.452 | 11.373 | 53.452 |
| 0.400 | 11.200 | 26.300 | 11.099 | 26.299 | 11.102 | 26.300 | 11.078 | 26.297 | 11.095 | 26.294 |
| 0.600 | 11.190 | 17.317 | 11.220 | 17.318 | 11.230 | 17.315 | 11.050 | 17.316 | 11.160 | 17.316 |
| 0.800 | 11.095 | 13.050 | 11.099 | 13.049 | 11.098 | 13.049 | 11.099 | 13.049 | 11.099 | 13.042 |
| 1.000 | 11.042 | 10.252 | 11.099 | 10.258 | 11.140 | 10.254 | 11.144 | 10.255 | 11.099 | 10.258 |

From the data in Table 1, applying the equation (1), the average velocity for each point was calculated, while the error was calculated with using the difference between the theoretical and experimental values. The results are presented in the first 3 columns of Table 2. To express a reliable value of the error in the dimensions measured quantity, a series of errors must be considered in the measurements made, which appear as a calculation error, although these events may be systematic or random, and not all have direct contributions to the measurement error, so this may vary due to the method and the instruments used to perform the data collection. For this case, the direct exit of the displacement of the nozzle was taken measured as a function of the time it takes to carry out a complete the full displacement (11 cm). It is important to clarify that all the random contributions to the error that can be considered due to imperfections in the motor rotation, resolution of the step of the motor, resolution of the step of the controller, leakage currents in the controller and resolution of the step of the worm, are not they contemplated directly since they are immersed in the direct error of the displacement of the nozzle. The error expressed is attributed to two sources that can directly contribute to the error, such as the contribution of the by measuring instruments (technical specifications) and statistical errors due to variations in the displacement of the nozzle. In equation (2) the following errors associated with the measurement are considered.

\[ E = E_r + E_{res} + E_{es} \]  

(2)

Where \( E \): Is the error of the measurement, \( E_r \): Error due to imperfect repeatability, \( E_{res} \): Error by resolution of the measurement instrument and \( E_{es} \): Error due to the specifications of the measuring instrument, (maximum error allowed by the instrument) [7]
2.3 Measuring instruments
To perform the time measurement, a CASIO digital timer model HS-80TW-1DF 100 with a resolution of 0.001 seconds and a maximum allowed error of 1% of the measurement was used. The distance was measured with a Mitutoyo brand vernier, model CD-S6 "CP, series 1964, with a resolution of 0.001 cm, and a maximum permissible error of 0.002 cm, according to the calibration certificate 00290 issued by the Dimensional Metrology Laboratory of the Technological University of Pereira.

2.4 Error uncertainty
To each error of in the measurement of the speed they are attributed a contribution of there is uncertainty given by the input data, said such contributions were calculated according to the equation (3)

$$u_e^2 = U_r^2 + U_{res}^2 + U_{es}^2$$  (3)

Where $U_e$: Is the combined uncertainty associated with the error of the measurement, $U_r$: Uncertainty due to imperfect repetitiveness, $U_{res}$: Uncertainty due to resolution of the measurement instrument $U_{es}$: Uncertainty due to the specifications of the measuring instrument [7]. Then, the calculation of the total combined uncertainty of the error was determined indirectly by means of the mathematical relationship that involves the input magnitudes (distance and time) and the correlation of their respective uncertainties, as shown in equation (4).

$$u_c = \sqrt{\sum_{i=1}^{n} C_i^2 u^2(X_i) + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} C_i C_j u(X_i, X_j)}$$  (4)

Where $u_c$: Is the total combined uncertainty, $C_i$ and $C_j$: are coefficients of sensitivity of distance and time, $u(X_i)$: Combined uncertainty of the input variables, $u(X_i, X_j)$: Covariance between the uncertainties of the input variables [7]. To determine the relationship between the distance and time variables with respect to velocity, the covariance between the uncertainties of said such variables was calculated using equation (5).

$$u(X_i, X_j) = \frac{1}{n(n-1)} \sum_{k=1}^{n} (x_{ik} - \bar{x}_i)(x_{jk} - \bar{x}_j)$$  (5)

Where $n$: Is the number of input data, $X_i$ and $X_j$: They are the input data for the position and time, $\bar{x}_i$ and $\bar{x}_j$: It is the average of the distance and time data taken [7]. To express the uncertainty of the error with a 95% confidence, the coverage factor $K$ was calculated for each of the degrees of freedom according to equation (6).

$$u_{eff} = \frac{u_c}{\sqrt{\sum_{i=1}^{n} \frac{u_i^4}{\nu_i}}}$$  (6)

Where $u_{eff}$: the effective degrees of freedom for a 95% confidence level of the input quantities, $u_{ci}$: is the combined uncertainty of the input quantities, $u_i$: are the degrees of freedom for each one of the components of the uncertainty for each input variable, $N$: Number of components [7].

Having the calculation of the effective degrees of freedom, the respective value of $K$ can be obtained in the Student t distribution table with a confidence level of 95%. With the value of $K$, the expanded velocity uncertainty can be calculated, and the measured error expressed as shown in equation (7).

$$E = E \pm K \times u_c$$  (7)
3. Results
Table 2, shows a summary of the results obtained after having performed the calculations described in section 2.

An error of less than 10% of the input value was obtained, and a decreasing tendency is observed as the nozzle speed increases, as shown in figure 2. It is also observed that the behavior of the absolute error is within the maximum permissible error limits calculated for this process, with a confidence level of 95%.

Table 2. Estimation of the error, coverage factor and uncertainty of the error.

| Theoretical Speed (cmmin-1) | Experimental Speed (cmmin-1) | Error (Vt - Ve) | Maximum Error Allowed | K   | Expanded Uncertainty (cmmin-1) |
|-----------------------------|-----------------------------|----------------|----------------------|-----|-------------------------------|
| 0.200                       | 0.212                       | -0.012         | ± 0.020              | 1.96| ± 0.002                       |
| 0.400                       | 0.423                       | -0.023         | ± 0.040              | 1.96| ± 0.005                       |
| 0.600                       | 0.645                       | -0.045         | ± 0.060              | 1.97| ± 0.008                       |
| 0.800                       | 0.851                       | -0.051         | ± 0.080              | 1.96| ± 0.010                       |
| 1.000                       | 1.069                       | -0.069         | ± 0.100              | 1.96| ± 0.024                       |

Figure 2. Error trend when increasing the speed of the nozzle.

To determine how the accuracy of the speed variable speed influences the characteristics of the thin films obtained, deposits of titanium oxide were made applied on glass substrates and the behavior of the transmittance spectra for different deposited coatings was studied, under the same conditions, in order to analyze the repeatability and reproducibility behavior of the constructed AACVD equipment built for this experiment. The deposit conditions were: Substrate temperature 450 ºC, drag air temperature 40 ºC, drag air flow 0.400 L min⁻¹, number of layers 2, nozzle speed 0.600 cm min⁻¹ and 0.4 cm min⁻¹; the transmittance spectra were performed in the wavelength range of the visible spectrum (380 nm-780 nm) with a UV-VIS spectrophotometer (Evolution 220 Thermo Scientific).

With the speed of 0.600 cm min⁻¹, three deposits were made and the spectra were taken at a point located at the same distance from the upper edge of each substrate ‘Figure 3’, while with the velocity of 0.400 cm min⁻¹ took the transmittance spectra was taken at three different points of the sample in order to analyze the uniformity of the coating ‘Figure 4’. It can be seen in ‘Figures 3 and 4’ a similar behavior between the spectra for each speed, which depends directly on the microstructural composition, roughness and thickness of the coating, so this can be associated to the characteristics of the process’s repeatability and the uniformity of the deposited coatings.
4. Conclusions

It was determined that the velocity of the nozzle of the AACVD equipment constructed in the UTP presents oscillations lower than 10% of the programmed speed, which allows obtaining optically uniform coatings, given that the transmittance spectra taken in different places of the deposit had a similar behavior regardless of the programmed speed of the nozzle. Therefore, when checking the repeatability and reproducibility of the films grown, at least in the measurement of transmittance, it can be concluded that the equipment complies with the established standards to be used in the area of science and study of materials, and therefore will be useful in the science field.

The statistical study carried out performed to the AACVD team device allows to report reliable results to the scientific community, since it there is certainty of the reproducibility in the deposits that are made, having a confidence level of 95%. From the practice it was detected that when the speed presents variations greater than 10% of the one programmed, there is no uniformity in the growth of the films.

Acknowledgments.

The authors thank the UTP (Project No. 3-16-4) and the CONACYT-SENER Energy Sustainability Fund (Project No. 249855) for the financial support granted to carry out this work.

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