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Application of Taguchi Methodology for Optimization of Parameters of CVD Influencing Formation of a Desired Optical Band Gap of Carbon Film

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Abstract

Taguchi methodology has been applied to get an idea about the parameters related to the chemical vapour deposition technique, which influences the formation of semiconducting carbon thin film of a desired band gap. L9 orthogonal array was used for this purpose. The analysis based on Taguchi methodology suggests that amongst the parameters selected, the temperature of pyrolysis significantly controls the magnitude of band gap (46%). Sintering time has a small influence (30%) on the band gap formation and other factors have almost no influence on the band gap formation. Moreover this analysis suggests that lower temperature of pyrolysis (≤ 750 °C) and lower time of sintering (≤ 1 h) should be preferred to get carbon thin film with the desired band gap of 1.2eV.

Keywords : *Taguchi Methodology, Chemical vapour deposition, Semiconducting carbon, Camphor soot, Band gap determination*

1. Introduction

There are many parameters, which affect the nature of product formed by thermal chemical vapour deposition (CVD) process during the pyrolysis of hydrocarbon. These parameters could be temperature of pyrolysis, sintering time, gas flow rate, type of precursor, carrier gas, heating rate etc. Some of these parameters would actually influence the formation of carbon film with desired properties, like band gap. When the numbers of parameters are large as is the case with CVD process, number of the experiments to be carried out becomes very large. As a result, it becomes very time consuming to find out the optimum conditions, which could give the desired product. For optimization of experimental conditions to get the desired product, Taguchi methodology seems desirable. This method helps to give definite information about the weightage of parameters influencing the production of a desired product even by conducting much smaller number of experiments.

Taguchi's method has been highly effective and many companies worldwide have recognized its importance. This method designs experiments by orthogonal arrays. The orthogonal array can also examine major effects, which control the formation of desired product and cuts down experimental time and resources enormously. For example, a process requiring 4 influencing factors at 3 levels would normally require 3^4 i.e. 81 experimental runs, whereas Taguchi method of analysis system would give all information by carrying out only 9 experiments whereas to get similar observation conventionally one need to carry out 81 experiments [1].

1.1. Taguchi methodology

In Taguchi method the output of experiments is computed by the equation (Eq. 1) to find out the "signal to noise ratio" (S/N ratio). This ratio determines the dominance of a particular parameter for the formation of the desired product. Taking "nominal- the-best" objective, S/N ratio is calculated from the following expression [2]

$$S/N\ (dB) = 10\log_{10}\ (SSm - Ve)/rVe \qquad (1)$$

where $Ve = (SS_T - SSm)/r-1$
Sum of $Square_{Total}$ $(SS_T) = \Sigma Yi^2$
Sum of $Square_{mean}$ $(SSm) = r\ (Ym)^2$
r = 2, the number of repetition experiments with same level and parameters.

This method gives information about the parameter levels (like various temperatures used for pyrolyzing a hydrocarbon), which maximizes the product using "analysis of mean" (ANOM) and identifies relative importance of all parameters influencing in giving the desired product. For this purpose "analysis of variance" (ANOVA) is calculated by employing equations-2 [3].

$$\text{Sum of the Squares} = \Sigma N_l (m_i - < m_i >)^2 \quad (2)$$

where $m_i = (1/N_l)\Sigma \, S/N$ (3)

m_i represents the contribution of each parameter level to S/N ratio, <mi> is the average of m_i's for a given parameter and the coefficient N_l represents the number of times the experiment is conducted with the same factor level in the entire experimental region. Sum of the squares i.e., sum of squares of variances for all levels for a given parameter is obtained by using ANOVA. This term is divided by corresponding degrees of freedom (DOF = number of parameter levels minus 1) to derive relative importance (factor effects) of various experimental parameters by utilizing equation 4. ANOM gives the factor level m_i which tends to maximize the S/N ratio and predicts the optimum level. From these calculations, it is possible to predict with accuracy the parameter having maximum influence on the formation of desired product (output of ANOVA) and the level of a given parameter that maximizes the product (output of ANOM).

$$\text{Factor effect} = SoS / \{DOF \times \Sigma (SoS/DOF)\} \quad (4)$$

Several researchers [4-9] extensively made use of this technique in optimization of parameters. To the best of our knowledge for the first time this technique is being used to optimize parameters to get a desired optical band gap for carbon film by CVD process.

The design of an experiment involves the following steps: (a) Selection of independent variables which do not have interaction within themselves, (b) deciding the number of levels for each variables, (c) selection of an orthogonal array and (d) assigning the independent variables to orthogonal arrays.

For the purposes of present research, a standard L9 array was adopted. The L9 array allows four process variables to be examined on three different preset levels, making a total number of 9 experiments. For this purpose four parameters were chosen, with three levels for each variable parameter, which controls the properties of film (Table 1). The number of parameters and their respective levels, which fits into an orthogonal array of L9, is given in the Table 2.

2. Experimental

2.1. CVD Unit

The deposition unit (CVD unit) consisted of a quartz tube (40 inch long and 1inch diameter) fitted with standard joints on both ends, two tubular electric furnaces (one for vaporization of camphor, at lower temperature and other for pyrolysis of camphor vapors, kept at higher temperature) and an argon gas cylinder. The schematic diagram is shown in the Fig. 1. A quartz tube was inserted into the horizontal tubular furnace. From one end of the quartz tube, an alumina boat filled with desired quantity (0.3 g to 2.5 g) of camphor was introduced into it and placed at the center of the

Table 1. Parameters and levels for the deposition of carbon film by pyrolysing camphor

	Levels		
Parameters	Level 1	Level 2	Level 3
A. Pyrolysis Temperature	750 °C	900 °C	1000 °C
B. Vaporizing temperature of camphor	150 °C	180 °C	250 °C
C. Substrate placement in the furnace	Horizontal	Vertical	Slanting
D. Sintering time of carbon film at 750 °C	1h	2h	5h

Table 2. Orthogonal Array of the experiments including optical band gap obtained from each set of experiments and the corresponding S/N ratios obtained for each film. Mean S/N ratio is found to be 23.04

Expt. No	Pyrolysis temperature °C (A)	Vaporizing temperature °C (B)	Substrate placement (C)	Sintering time (D)	Band gap (eV)	S/N ratio (dB)
L1	750	150	Horizontal	1h	1.18	30.43
L2	750	180	Vertical	2h	1.23	30.79
L3	750	250	Slanting	5h	1.18	30.43
L4	900	150	Vertical	5h	0.98	14.83
L5	900	180	Slanting	1h	0.48	22.56
L6	900	250	Horizontal	2h	0.45	22.56
L7	1000	150	Slanting	2h	0.47	22.56
L8	1000	180	Horizontal	5h	0.63	5.863
L9	1000	250	Vertical	1h	0.83	27.36

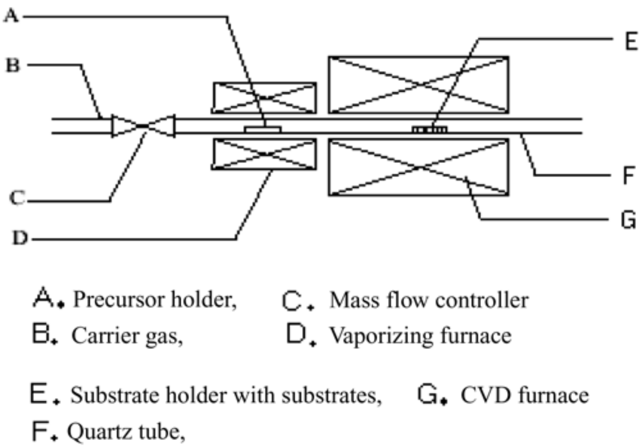

Fig. 1. Schematic diagram of experimental set up used in CVD process.

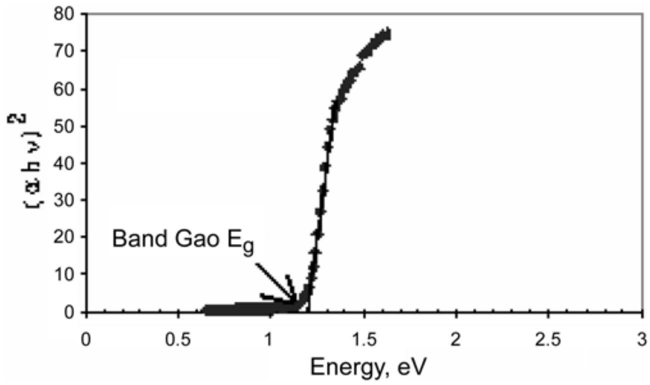

Fig. 2. A typical absorption graph obtained with carbon film prepared at 750 °C (pyrolysis temperature), 180 °C (vaporizing temperature), 2hours (sintering time), and vertically placed substrate with etch, showing by arrow the optical direct band gap of the same sample.

vaporizing furnace. The same end of quartz tube was connected to a flow meter and an argon gas cylinder. The gas flow rate was maintained between 5-20 sccm. Substrates were introduced from the opposite end of flow meter and then kept inside the tube at the center of the pyrolyzing furnace. Different substrates were used in the deposition process for different measurements. Quartz and n-silicon, (100) orientation, were used and kept in different fashion for deposition, such as horizontal, vertical (making parallel to the direction of flow of gas) and slanting. The substrates were cleaned with acetone and trichloro ethylene in ultrasonicator (28 KHz) for 2 minutes. They were etched with 1:10 HF for 20-30 sec. The cleaned substrates were immediately put inside the reaction tube. The substrates were of 1 cm × 1 cm dimension. The distance between the hydrocarbon source (camphor) and the substrate was kept 40-50 cm apart for all the experiments. Both ends of quartz tube were closed with the help of proper standard joints. Flushing with argon gas was done for 10 minutes to remove air/oxygen from the quartz (reaction) tube and then the furnace containing the substrates in the quartz tube was switched on.

After reaching the pyrolysis temperature, the furnace-containing precursor was switched on and temperature was set for vaporization of camphor. By thermal chemical vapor deposition method, camphor was pyrolysed at different temperatures (Table 1). On completion of pyrolysis, samples were kept inside the furnace for sintering for different duration (Table 1) at 750 °C. When furnace was cooled, films were removed and their optical band gaps were measured.

3. Results and Discussion

3.1. Optical band gap measurement

The transmittance and reflectance of carbon films were studied in the range of 500 nm to 1900 nm using single beam spectrometer at room temperature.

The band gaps of the films were estimated [10] using the formula.

$$\alpha h\nu = A\,(h\nu - E_g)^{n/2} \qquad (5)$$

where n = 1 for a direct and n = 4 for an indirect band gap.

From the transmittance and reflectance data the optical band gap (direct) of carbon film was calculated and found to vary from 0.4 eV to 1.25 eV depending on the deposition conditions (Table 2). The Fig. 2 shows a typical plot for calculation of direct band gap of a carbon film deposited at a pyrolysis temperature of 750 ºC and camphor vaporization temperature of 180 ºC. The intercept (shown by arrow) was taken as the band gap the material. Similar graphs were plotted for all other samples and from the intercept on the x-axis band gaps were calculated. These values are shown in Table 2.

3.2. Taguchi optimization calcultations

Calculation of a typical result is discussed here to elucidate the Taguchi method of Analysis. Results of one set of experiment (Table 2) are selected for this purpose. In order to get information on parameters influencing maximum for getting a desired product (here it is band gap), there is a need to calculate S/N ratio for each control factors and their levels. For this purpose we need to evaluate S/N using equation 1. Thus SSm and SS_T are calculated as follows:

$$SSm = r\,(Ym)^2 = 2 \times (1.175)^2 = 2.76125$$
$$SS_T = \Sigma Y_i^2 = (1.15)^2 + (1.2)^2 = 2.7625$$
$$Ve = (SS_T - SSm)/r - 1 = (2.7625 - 2.76125)/1 = 0.00125$$

Putting the respective value in the Equation 1 we get the

Table 3. Effect of various selected parameters on the optical band gap of carbon thin film

FACTOR	Average by factor level (dB)			Degrees of Freedom	Sum of Mean Squares ≅ SoS	% Factor effect
	1	2	3			
A. Pyrolysis Temp	30.55	19.98	18.59	2	256.6	46
B. Vaporising Temp	22.6	19.74	26.78	2	75.21	14
C. Substrate Placement	19.62	24.32	25.18	2	53.74	10
D. Sintering. Time	26.78	25.3	17.04	2	165.2	30

S/N ratio

$$\text{i.e., S/N ratio} = 10 \log (2.76125 - 0.00125)/2 \times 0.00125$$
$$= 10 \log 1104 = 10 \times 3.0429 = 30.429.$$

In this fashion S/N for each level is calculated and shwon in Table 2.

The sum of square (SoS) is calculated from equation 2. Let's take the case of temperature of pyrolysis to elucidate this calculation. There are three average factors levels values i.e. for m_i (calculated by using equation 3): 30.55, 19.98 and 18.59; from which average $<m_i>$ is calculated to be 23.04. Since this experiment was done three times, Ni = 3. Putting these values in equation 2, we get the value of SoS for pyrolysis temperature as:

$$\text{Sum of squares (SoS)} = 3\,(30.55 - 23.04)^2 + 3\,(19.98 - 23.04)^2 + 3\,(18.98 - 23.04)^2 = 256.6$$

Like wise one can calculate SoS for other factors (i.e., vaporizing temperature, substrate placement and sintering time). Results of these calculations are given in Table 3

Now it is possible to plot a graph of S/N ratio for each parameter (i.e., pyrolyzing temperature, vaporizing temperature, position of substrate and time of sintering). For this purpose we take the mean value of S/N (i.e. 23.04, Table 3) as the base line to show which parameter has better impact on the desired product. Parameters giving value lower to mean S/N suggests that it has less effect than those that gives higher than mean value to get the desired product. This result is plotted in Fig. 3. It appears from this graph that pyrolyzing temperature has pronounced effect on giving band gap of desired value. Moreover it also suggests that lower temperature of pyrolysis is better than higher temperature.

In order to know quantitatively about the factor, which has more pronounced effect on producing the desired product (i.e., band gap), percentage factor is calculated by using equation-4. This is done as follows:

SoS = 256.6,

Degree of freedom = 2 (i.e., number of parameter's level minus 1),

$$\Sigma\,(\text{SoS/DOF}) = 256.6/2 + 75.21/2 + 53.74/2 + 165/2 = 275.25$$

$$\text{Factor effect} = 256.6 / (2 \times 275.24) = 46.$$

Likewise one can calculate for other two parameters (Table 3). Thus, one can predict that amongst all the

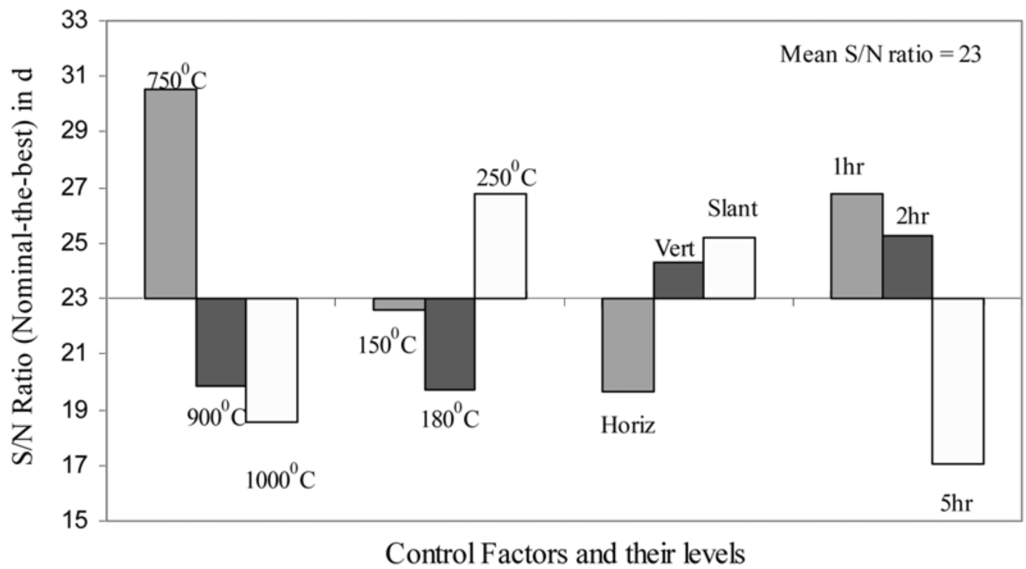

Fig. 3. Relative response of various parameters and their corresponding levels on optical band gap of carbon film prepared by pyrolysis.

variables temperature controls 46% and sintering time is the next parameters controlling to the extent of 30% in getting a carbon thin film with a desired band gap of 1.2 eV by pyrolysis of camphor. Other parameters have less effect on producing desired product. Taguchi method thus has been able to give such vital information by conducting only 9 sets of experiments instead of carrying our 81 experiments, if we had to follow the conventional method of analysis.

4. Conclusion

Taguchi methodology has been successfully applied to find out the parameters of CVD process, which controls the formation of semiconducting carbon of band gap 1.2 eV. Taguchi analysis has suggested that amongst the various parameters, temperature has 46% effect on controlling the production of carbon film and sintering time has 30% impact on the production of desired product, while all other parameters taken together have only 26% impact on controlling the production of carbon semiconductor. Moreover, this analysis also suggests that trend in which temperature and sintering time have pronounced impact in producing the desired product. For both these parameters lower temperature and lower time of sintering favours the formation of the desired product. All these information could be obtained by carrying out only 9 sets of experiment as compared to 81 that would have normally required if conventional method were to be adopted.

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