A controlled atmosphere tube furnace was designed for thermal CVD

M Rashid1, 3, J A Bhatti2, F Hussain1, M Imran1, I U Khawaja1, K A Chaudhary1 and S A Ahmad1
1Department of Physics, The Islamia University of Bahawalpur Pakistan 63100
2Pakistan Vacuum Society, Islamabad, Pakistan
3Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542

E-mail: rapakistana@yahoo.com

Abstract: High quality materials were used for the fabrication of hi-tech tube furnace. The furnace was especially suitable for thermal Chemical Vapor Deposition (CVD). High density alumina tube was used for the fabrication of furnace. The tube furnace was found to have three different temperature zones with maximum temperature at central zone was found to be 650°C. The flexible heating tape with capacity of 760°C was wrapped on the tube. To minimize the heat losses, asbestos and glass wool were used on heating tape. The temperature of the tube furnace was controlled by a digital temperature controller had accuracy of ±1°C. Methanol was taken as the representative of hydrocarbon sources, to give thin film of carbon. The a-C: H structure was investigated by conventional techniques using optical microscopy, FT-IR and SEM.

1. Introduction

In the mid seventeenth century the competition to find an ideal and convenient thermometer was under discussion. Galileo began to use and modified the Florentine thermometer. The lower fixed point (ice point) is temperature at which water and ice coexist in thermal equilibrium under a pressure of 1 atm. upper fixed point is the temperature at which water and steam coexist in equilibrium under a pressure of 1 atm [1]. By bonding two metals with different coefficient of thermal expansion, achieved a strip that bends in reaction of temperature change. It is widely used in the home furnaces, being switched ON or OFF by thermostat [2]. Theory of thermocouple based on Seebeck effect. Seebeck’s finding has resulted in possibly the most general method of temperature measurement. The See beck effect is observable as a voltage potential that occurs when there is a temperature gradient along the length of a conductor. Copper-constantan thermocouples have been used for several years and it is called the T-type. Good quality copper has abnormally attractive properties for use either in thermocouple or as a standard material for thermoelectric assessment purposes. The only disadvantage of copper is its tendency to oxidize quickly at high temperature. Due to this restriction it becomes difficult to use it in air above 400°C. Because of the oxidation trouble small diameter exposed copper wire has a much shorter useful life than that of larger size. There is a small amount of thermocouples that can be tolerated in reducing atmosphere, so iron-constantan is mainly important in this respect and it is called J-type. A base metal thermocouple with Chromel-Alumel is called K-Type thermocouple that was developed by the Hoskins manufacturing company. In short, a chromel type wire at room temperature that has been recently hard drawn, greatly cold worked, or reduced from high temperature state is in a fully disordered condition [3]. A device which is used to provide controlled temperature for the heat treatment of material is called furnace. It is an enclosed chamber in which heat is produced for heat building, destroying refuse, smelt or refine ores, etc [4].
CVD is a deposition method where chemical precursors are elated in the vapor phase to decay on a heated substrate to form a film [5]. The formation of films depends on the materials and the condition of reactor. These films may be polymers, amorous carbon and glassy carbon. It has become the most important technique of film deposition. It offers the advantage that operates at low temperature. Two types of reactors are widely used in this process. Hot wall reactor and cold wall reactor. In hot wall reactor, a heater surrounds the reaction region. The heater can be heated by electrical resistance [6]. The deposition is not well-organized since the hot walls are coated as well as the substrate. The hot wall reactor is perfect for the situation where the effect is exothermic. The high wall temperature stops the unwanted positions on the reactor walls. Horizontal and vertical tube furnaces are mostly used for CVD. Hot wall reactor is called Tube furnace. CVD synthesis is achieved by putting a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, in order to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene. The aim of present work is to study carbon film on silicon and glass substrate.

2. Experimental results

The grain size of polycrystalline material is from 1 to 5 microns and its density is 3.95 g/cm². The water absorption is zero percent and its hardness is about 2000 Vickers. The value of dilatation coefficient at 2000°C is 8.4×10^-6 °C^-1 and its thermal conductivity is 40 (W/m-K) at 20°C. Alumina (Al₂O₃) has been used as tube reactor and having corundum crystalline structure. It has excellent wear resistance, electrical insulation and good thermal conductivity. It has high hardness compression strength. It is used in ballistic amour, electronic substrate and high voltage insulators in element formers. In thermocouple two different metals having dissimilar number of free electron at same temperature are used. When the hot region is moved along the conductors it passes through area where the metals are connected. There is difference in electron density and therefore difference in charge circulation. Due to this current flow throughout millimeter, as free electrons try to move into equilibrium. This movement will continue until the heat energy is applied. The voltage calculated by this charge distribution is called EMF and proportional to temperature. Asbestos used as a heat resistance in furnaces, insulation on pipes, boiler and hot water tanks. Insulation used to stop heat loss [7]. Glass wool is the superb thermal insulator and the best thermal resistance. Therefore it reduces energy utilization and also reduces variations of temperature in tube furnace [8]. The temperature controller is made with PID (Proportional, Derivative and integral) controller for controlling the temperature. As complete connection and parts that are used in the construction of tube furnace are shown in figure 1.

The tube that is used for the construction of furnace having internal and external diameters of 17 and 24 mm and the length is 500 mm. The ends of the tube are closed by the Teflon covers. The crucible is used for placing the samples in the furnace at different zones. It is divided into the three zones in order to get readings as shown in table 1. Thick insulation divides this trapped air into a greater number of split cells, slowing exchange and the rate of heat flow. The metal sheet is used to pack all these materials and gives the absolute shape to the furnace. The heat loss that controlled by insulation can be seen by the figure 2. Temperature was measured by using the Chromel-Alumel (K type) thermocouple. It gives linear behavior result than copper-constant (T type) and iron-constantan (J type) thermocouples. The comparisons of all these types of thermocouples are shown in the figure 3. The experiment was performed at room temperature and the temperature of the room was 27 °C.

In order to observe the micron size crystals smoothness of the surfaces and crystal boundaries, an optical microscope must be used. A modern Scanning electron microscope (SEM) provides an image resolution typically between 1 nm and 10 nm, not as good as the TEM but much superior to the light microscope. In addition, SEM images have a relatively large depth of focus: specimen features that are displaced from the plane of focus appear almost sharply in focus [9].
Atmospheric pressure thermal CVD (APTCVD) has many possible advantages over other forms of coating technology, which can give important marketable advantages in definite areas of glass coating technology. This is the simplest and widely used method. Glass or silicon is commonly used as a substrate. Heating is normally skilled by use of resistive heating. A hot wall reactor is known as isothermal furnace in which substrate is located. In this reactor, many substrates are deposited at a time. The whole tube is heated and exact temperature control can be achieved with accurate furnace design. A drawback of hot wall design is that deposition occurs on the walls of the tube plus on the substrate. As a result, hot wall reactor must be cleaned to decrease the cracking of particles from the walls which may infect the substrate. The pressure factor of the reactor depends on rate restrictive step of deposition. The tube is radially isothermal and thermal diffusion length is greater than the radius of the tube. Heat can simply pass through by conduction from the wall of tube to central region. The radial temperature remains constant if temperature of the tube wall is constant [10]. Complete experimental arrangement for the inert atmosphere thermal CVD is schematically shown in figure 4. Air is mainly composed of nitrogen, oxygen, and argon, which together constitute the "major
gases" of the atmosphere. The remaining gases are referred as "trace gases, often among which are the greenhouse gases such as water vapor, carbon dioxide, methane, nitrous oxide, and ozone. Thick insulation divides this trapped air into a greater number of split cells, slowing exchange and the rate of heat flow. The metal sheet is used to pack all these materials and gives the absolute shape to the furnace. Typical experimental conditions employed in the present study are summarized in table 2.

Table2. Experimental conditions for the deposition of carbon film.

| Sr. No. | Item                        | Value          |
|---------|-----------------------------|----------------|
| 1       | Source material             | CH3OH          |
| 2       | Carrier gas                 | Ar             |
| 3       | Maximum temperature         | 650°C          |
| 4       | Temperature accuracy        | ±1°C           |
| 5       | Crucible material           | Alumina        |
| 6       | Pressure                    | Atmospheric    |
| 7       | Substrate                   | Glass & Silicon|
| 8       | Type of Film                | Carbon         |
| 9       | Sintering time              | 1-30min        |
| 10      | Ar flow rate                | 2ml / min      |
| 11      | Bath temperature            | 60°C           |
| 12      | Glass flask temperature     | 500°C          |

Figure4. Complete experimental setup of atmospheric pressure thermal CVD

3. Results

Some important specifications are given below in table 3.

3.1. Optical microscopy

To analyze the photos captured by the optical microscopy, their structures are explained. At 400°C, almost hexagonal structure was observed; the film deposition was uniform as shown in figure 5. At 550°C, the clear hexagonal structures are shown in figure 6. Hexagonal orientation was observed at the surface and it had poly crystalline structure with a combination of (111) and (100) surfaces. The film distribution was uniform. Film was so thin that its thickness could not be measured by the optical microscope.

Table 3. Specifications of the tube furnace.

| Sr. No. | Item                                | Value                |
|---------|-------------------------------------|----------------------|
|         | Temperature range                    | 0 - 760°C            |
|         | Thermocouple                         | K-type (Chromel-Alumel) |
|         | No. of Zones                         | Three                |
|         | Length of each Zone                  | 200mm, 100mm, 200mm  |
|         | Internal Diameter of Tube            | 17mm                 |
|         | External Diameter of Tube            | 24mm                 |
|         | Length of the Tube                   | 500mm                |
|         | Controller Diameter                  | 8100mm²              |
|         | Length of Crucible                   | 80mm                 |
|         | size of Crucible                     | 10mm                 |
|         | Temperature Display                  | Digital              |
|         | Accuracy                             | ±1°C                 |
|         | Power                                | 220VAC / 50Hz        |
|         | Both Ends                            | open or Closed (Teflon Caps) |
3.2. Inter atomic bonding using methanol as source material

Fourier Transform Infrared (FTIR) is the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. Figure 7 shows the IR spectrum of the sample when the carbon film was deposited on Si (100) substrate at 500ºC for 30 minutes. The upward peaks are due to the loss of reagents while negative peaks reflect the generation of products during the oxidation of methanol within the thin layer transparent cell. The band at 3724 cm\(^{-1}\) can be assigned to symmetrical stretching vibration mode of O-H from isolated terminal silanoals (Si-OH) groups. The peak at 1700 cm\(^{-1}\) was a resultant of oscillation of C-O double bond in carboxylic group. The bands at 1644 cm\(^{-1}\) and 1570 cm\(^{-1}\) are due to stretching of carboxyl group C-O.

Figure 8. shows IR spectrum of the sample when the temperature was 600ºC and deposition time was 20 minutes. The Pears of strong IR bands at 2862 cm\(^{-1}\) 2964 cm\(^{-1}\) due to methyl (CH\(_3\)) symmetric and asymmetric stretching demonstrate the presences of methanol and evidence of successful methanol adsorption. The presence of C-H stretching band at 2811 cm\(^{-1}\) that associated with methoxy (O-CH\(_3\)) shows generation of methoxy species due to methanol adsorption. The small upward peaks at 1450 cm\(^{-1}\) also reflect the depletion of methanol during oxidation process. In figure 7. and figure 8., the band at 2324 cm\(^{-1}\) was due to the atmospheric CO\(_2\). Particularly at location, where large numbers of vacancies are present, methanol can dissociate all its hydrogen resulting in the generation of CO. The samples were prepared at various time duration, only effect on the transmittance of the peaks and the wave number of the peaks almost same. FTIR spectrum shows that there are many hydroxyl groups with oxygen atom distributing on the surface of carbon microspheres.
3.3. Surface studies of carbon film

A series of experiment was performed to investigate the deposition of carbon on Si (100) using methanol as a source material and argon as a carrier gas. These experiments were performed at deposition temperatures ranging from 350 °C to 600 °C. There was no film deposit on the samples that were operated below 350 °C. Figure 9(a), (b) and (c) show the results when the film was deposited at 400°C, 500°C and at 600°C respectively.

![Figure 9. SEM images of deposition of carbon film (a) at 400°C(b) at 500°C and (c) at 600°C.](image)

4. Conclusion

A moderate temperature, in the range, of 0 – 750 °C was produced by a flexible heating tape in a high density alumina tubing. The temperature was controlled by a digital temperature controller with an accuracy of ±1°C up to 650 °C. High performance materials were used for the construction of tube furnace. To illustrate the usefulness of the furnace, a variety of materials were chosen. Specifically Silicon (Si), Barium Titanate (BaTiO₃), Methanol (CH₃-Oh), Yitrium Barium Copper Oxide (Y₁Ba₂Cu₃O₇) and Calcium phosphate (Ca₅P₂O₇) were selected as the representatives of their respective families Semiconductors, Ferroelectrics, Hydrocarbons, Superconducting and Bio-ceramics respectively. All the above said materials were fabricated in the tube furnace successfully and characterized by standard techniques like OPTICAL MICROSCOPE, XRD, FTIR and SEM but the present research discusses hydrocarbon only.

References

[1] Tippens P E 1978 Appl. Phys. 2 4
[2] Drever R W P 1983 Appl. Phys. B 31 97-105
[3] Kinzie P A 1973 Thermocouple Temperature Measurements (R. David Moore and Company) pp1-35
[4] Mullinger P and Jenkins B 2008 Industrial and Process Furnace (Butterworth- Heinemann)
[5] Larsson I A S, Elianne M L, Lundstrom T S, Daniel M V and Simon T 2009 Kiln Aerodynamics visualization of merging flow by usage of PIV and CFD Seventh International Conference on CFD in the Minerals and Process Industries CSIRO (Melbourne, Australia 9-11)
[6] Barron A R 1997 J. Chem. Mat. 4 967
[7] Wilson A 2010 Avoiding the Global Warming Impact of Insulation (SAP 2009 England)
[8] Carman P C 1937 Fluid flow through a granular bed Transactions of the institution of chemical engineers (Electronic Materials Vol 15) ed E Scholl (London: Chapman and Hall) pp 150- 167
[9] Goodhew P J, Humphreys J and Richard B 2008 J. Materials 29 pp 43-53
[10] HsinTien C, Shiw C, Chung T 1998 J. Elsevier sci. 17 2190