Chapter 2

Experimental set-up for the synthesis of HDLC films on various substrates at room temperature
2.0 Introduction

Over three decades of research in science and engineering technology have been performed into understanding, developing, and applying low pressure diamond deposition/coating onto the materials of immense interest for industrial, medical and technological fields. A unique method at low pressure diamond synthesis is designated to as the ‘New Diamond Technology’ to discriminate it from ‘High Pressure and High Temperature’ (HPHT) diamond synthesis. In new diamond technology, at low atmospheric pressure and at ordinary temperature, the typical sources of carbon, viz. methane, carbon monooxide, is changed by chemical vapor deposition of diamond. Technologically, the layers of diamond over large surface area can be synthesized. The deposited diamond layer on the wide variety of host materials is accompanied by the exceptional properties of diamond (viz. extreme hardness, high thermal conductivity, high corrosion resistant, low coefficient of friction, low infrared and microwave absorption, and wide band semiconductor) suitable for a particular applications. The deposition of diamond films using new technology is made possible by an improved scientific knowledge and by the research and development of CVD systems especially designed for the deposition of diamond. There are few efficient methods for making low pressure diamond depositions. To correlate the quality of the films and for better understanding of the characteristic properties of the films, the deposition conditions, methods of depositions, and the type of equipments are needed to be studied immensely [94].

Phase diagram of carbon is shown in Figure 2.1. From the diagram it is seen that diamond is the stable form of carbon at high pressure (thousands of atmospheres) and high temperatures (thousands of degree celsius). It may be seen that graphite is the stable form of carbon under ordinary temperature and pressure. The artificial synthesis of diamond from graphite is under the conditions of ~55000 atm. and temperature ~2000 ⁰C was first reported by General
Electric group viz. Bundy et al. in 1955 [95]. A metastable state is not the minimum energy arrangement of the atoms. Diamond at ordinary temperature and pressure is metastable state of carbon. However, carbon atom in diamond lattice does not spontaneously convert to graphite under low pressure and temperature. Therefore, under suitable deposition condition, synthesis of diamond seems to be feasible from nascent carbon containing species under metastable conditions and thus inviting the new era in the preparation of diamond film coatings. The possibility of new applications of diamond films are mainly due to the exceptional properties of diamond.
Table 2.1 Electronic Configuration of Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Electronic Configuration</th>
<th>Pictorial Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>1s¹</td>
<td>↑</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>1s² 2s² 2p²</td>
<td>↑↓ ↑↑ ↑ ↑</td>
</tr>
</tbody>
</table>

In order to explain the formation of four equivalent covalent bonds by carbon it was assumed that prior to reactions, one of the two equivalent 2s electrons of carbon is promoted to the third 2p level giving the excited state configuration:

\[
\begin{array}{cccc}
\uparrow & \uparrow & \uparrow & \uparrow \\
1s & 2s & 2p & 2p
\end{array}
\]

Then the mixing of one 2s and three 2p orbitals provide the four equivalent sp³ hybrid orbitals with one electron in each. All the bond lengths and angles are equal when bonded to the same atoms.

![Figure 2.2 Spatial arrangements of carbon sp³, sp² and sp hybrid orbital (σ bonds)](image)

Carbon forms variety of crystalline and disordered structures because it is able to exist in three hybridization states, viz. sp³, sp², and sp (Fig. 2.2). In the sp³ hybridization, as in diamond, a carbon atom forms four strong σ bonds along the tetrahedral directions using four valence electrons. In the three fold coordinated sp² hybridization, as in graphite; three valence
electrons forms trigonally directed planer sp$^2$ orbital’s which forms $\sigma$–bonds in a plane. The fourth electron of the carbon atoms lies in a p$_\pi$ orbital which forms a weaker $\pi$-bond with the neighboring atoms. This $\pi$ bond lies normal to the $\sigma$–bonding plane. In sp hybridization, two of the four valence electrons enter $\sigma$–orbital’s, each forming a $\sigma$–bond along the X-axis and other two electrons enter p$_y^\pi$ and p$_z^\pi$ orbital’s in Y and Z direction make two $\pi$-bonding with orbital of neighboring atoms. The $\pi$-bonds are perpendicular to each other and also perpendicular to the $\sigma$–bond plane.

2.1 History of ‘Diamond’ and ‘Low Pressure Diamond Synthesis’

The synthesis of ‘Diamond’ has been undertaken considering the two principal facts in the primary stage of diamond synthesis. They are (a) diamond and charcoal are made from same elemental carbon and (b) diamond is denser than charcoal. Therefore, compression at high pressure seems to be a viable route to achieveing diamond synthesis. Lewis and Randall [96] in 1915 showed that at room temperature and ~ 1 GPa pressure, diamond-graphite equilibrium exist. Soon after that, General Electric Corporation in 1955 first sucessfully synthesized diamond from graphite in molten metals at temperature 1700-2000 K and pressure from 7-10 GPa. Willam G. Eversole [97] for the first time proposed that the synthesis of diamond at low pressure from carbon monoxide on a diamond seed, considering the regions of metastability of diamond and graphite (Fig. 2.1 dashed line). Lander and Morrison et al. [98] crucially recognized the critic al and significant role of hydrogen in epitaxial growth of diamond on diamond. Hydrogen creates a kinetic barrier to graphitization. Angus and his coworker [99] showed the role of hydrogen, the machanism for diamond growth, kinetics, and proposed the growth on surface sites. The numerous research established the unique and unmatched role of hydrogen which etched out the graphitic carbon structure preferentially than diamond and hence supress the nucleation and growth of
graphite. Consequently this results in the synthesis of diamond at low pressure inspite of its thermodynamic unstability.

2.2 General methods for Diamond Like Carbon Synthesis

2.2.1 Physical Vapor Deposition (PVD):

Physical Vapor Deposition (PVD) is a general term used to describe variety of methods to deposit thin films by the condensation of a vaporized form of the desired film material onto various surfaces (e.g., onto semiconductor wafers). The coating process involves purely physical process for example high temperature vacuum evaporation. Few typical examples are given below

- **Cathodic Arc Deposition:**
  
  In which high power arc discharge at the target materials blasts away some into highly ionized vapor.

- **Pulsed Laser Deposition:**
  
  In which a high power laser ablates materials from the target into a vapor.

- **Sputter Deposition:**
  
  In which a glow discharge bombards the material sputtering some away as a vapor.

- **Electron Beam Physical Vapor Deposition:**
  
  In which material to be deposited is heated to a high vapor pressure by electron bombardment in high vacuum.

2.2.2 Chemical Vapor Deposition (CVD):

Chemical Vapor Deposition (CVD) is a general term used to describe variety of methods to deposit thin films from one or more volatile precursors, which react
and/or decompose to produce the desired deposit onto various surfaces (e.g., onto semiconductor wafers). Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber. Following are the different types of CVD methods

- **Atmospheric pressure CVD (APCVD)**
  Chemical vapor deposition at atmospheric pressure

- **Plasma Enhanced Chemical Vapour Deposition (PECVD)**
  CVD process that utilize plasma to enhance chemical reaction rate of the precursors. PECVD process allows deposition at lower temperature (e.g., Room temperature).

- **Microwave Plasma-Assisted CVD (MPCVD)**
  Microwave is used to create the plasma

- **Metalorganic Chemical Vapor Deposition (MOCVD)**
  Metalorganic chemical vapor deposition based on metalo-organic precursors e.g., trimethyl gallium
Figure 2.3 Ternary phase diagram of bonding of amorphous carbons. The corners represent diamond (sp$^3$), graphite (sp$^2$) and hydrogen (H).

It is very convenient to display the composition of various forms of carbon films (C-H) on a ternary phase diagram as shown in Figure 2.3. The different deposition methods have been developed to produce carbon film with different degree of sp$^3$/sp$^2$ bonding. A range of deposition methods are able to reach in the different locations of the ternary phase diagram is also shown in Figure 2.3. For example, PECVD is able to reach into the interior of the triangle. In this chapter, brief introduction is given to HDLC film depositon using PECVD technique.

2.3 PECVD System

2.3.1 Description of the System

The experimental facility for synthesis of HDLC thin film at Saha Institute of Nuclear Physics is shown in Figure 2.4, and the schematic block diagram of the PECVD instrument is
shown in Figure 2.5 to explain the operation procedures. This instrument is a state-of-art single chamber deposition system, which is indigenously designed and developed by my guide, Dr. Nihar Rajan Ray, to produce high quality PECVD films. Two major gas sources are available but we have used only one for our work which is methane (CH₄) for deposition of the film. The system also possesses other gases viz. Hydrogen (H₂), Helium (He), and Nitrogen (N₂). The hydrogen gas is used for both the pretreatment and deposition processes. The role of hydrogen and importance of hydrogen has been described in introduction part of chapter 1. The nitrogen is used as a purging gas and must be utilized during the deposition process to prevent the explosion. These gases are introduced into the chamber in a controlled manner using a Mass flow controller (MFC) units. The Si(100) substrates of ~10 mm diameter and 1 mm thick disc are always cleaned using isopropyl alcohol with a ultrasonic bath for 10 minutes, and then ultrasonically cleaned with milipore water and then used for deposition of the films. The loading and unloading of substrates can be done via a hinged door port located at the front of the deposition chamber. The other ports are provided in the chamber to view the substrate and progress during the deposition. Those ports can be used in future for analysis of plasma emission spectra and electron temperature, electron density and electric potential of the plasma using a Langmuir probe. The substrates were always placed on the cathode (marked as 1 in Fig. 2.5). The cathode is 250 mm dia. of metallic electrode connected to the RF matching circuit and power supply. The substrate can be floated or biased, depending on bias requirement on the substrate. The system consists of two types of pumping systems. Mechanical pump is first, switched on for making the chamber pressure from atmospheric to ~ 0.1 mbar. Small traces of oil are absorbed by the chemical filter which prevents the contamination during the processes of deposition. Subsequently a Roots pump is switched on when the pressure is ~0.1 mbar and continued until the pressure reaches desired value (~10⁻⁴ mbar). The exhaust connection of the chamber rotary vane pump is connected to an effluent
scrubber system. As a safety feature, a diaphragm pump is used to ensure that air is never pumped into the gas scrubber system. The RF power is generated from a RF generator. There is a RF matching circuit that optimizes the input power on the deposition chamber. The sample, cathode plate and related RF electronic equipments are cooled with the help of the closed loop cooled water circulation system.

2.3.2 Description of System Operation

Our PECVD facility is a typical representation of deposition system with all components required for the synthesis of HDLC film is shown in Figure 2.4. The violet hydrogen plasma is clearly observed through the front glass view port of the system. For a typical deposition, we used the following gases: Helium (He, 1500 SCCM) (SCCM-Standard Cubic Centimeter Per Minute), hydrogen (H₂, 500 SCCM) and methane (CH₄, varying 90-10 SCCM). The substrate in most cases is Si(100) or sometime quartz, stainless steel, carbon foam etc. To run the system and deposit films, the chamber is evacuated through mechanical and roots pumps and cooled the substrate and electronic parts using closed loop cooled water circulation system. Then the gases are introduced into the chamber through MFC using a electronically controlled system. The chamber pressure is controlled by electronically adjusting the valves opening. The hydrogen gas is first introduced in the chamber for removal of any surface contamination and oxide layer onto the substrate. This etching of mirror polished Si(100) substrate of 10 mm diameter for 15 min is carried out in a pure hydrogen (H₂ flow rate ~ 500 SCCM) plasma (light pink in color), at a pressure of 0.193 mbar, produced by 30 W RF forward power producing dc self-negative bias (~ -200V) with a impedance matching circuit, to remove any oxide layer from the surface of Si(100). The in-situ biased enhanced nucleation (BEN) process using helium (He flow rate ~1500 SCCM) plasma is produced by 50 W RF power producing dc self-negative bias (~ -200 V), with H₂ (flow rate ~500 SCCM) and CH₄ (flow rate~50 SCCM) gases at a total pressure of 0.756 mbar and at substrate
temperature \sim 14^\circ C, for 30 min deposition time. Table 2.1 list the experimental parameters used for the deposition of various films.

**Experimental facility for synthesis of HDLC at SINP:**

Figure 2.4 Experimental facility for synthesis of HDLC at Saha Institute of Nuclear Physics

*Figure 2.4 Experimental facility for synthesis of HDLC at Saha Institute of Nuclear Physics*

*Picture of our Plasma Enhanced Chemical Vapor Deposition (PECVD) Instruments for HDLC Synthesis. This instrument is indigenously developed by Prof. N. R. Ray, Plasma Physics Division, Saha Institute of Nuclear Physics. For this work, Prof. Ray got appreciation by Dr. A.P.J. Abdul Kalam, in the year of 2006.*
Figure 2.5 Schematic block diagram of the PECVD Instrument

Different parts of the System

1 – Cathode

2 – Anode

3 – RF-Matching Circuit

4 – RF Power Supply

5 – Drain (Collector)

6 – Vacuum Pumps (Mechanical and Roots pump)
The mechanism for plasma formation is discussed herein. In the beginning of the process, it is assumed that there are some electrons already exists inside the chamber. Under the acceleration of high voltage from the RF generator (13.56 MHz), they also oscillate very quickly among the gaseous atoms viz. He. Within very short time, they attain very high energy and momentum which are then transferred to the atoms to ionize them. The resulting electrons then follow the same path, i.e. further ionize the atoms. This multiple ionization process proceeds very fast and resultant plasma is formed. The power supply from a RF generator is coupled through a capacitor to the cathode as shown in Figure 2.5. As a result, a negative dc self-bias is induced on the cathode and on an ungrounded substrate Si(100). The bias on the cathode is controlled through RF impedance matching circuit and kept constant at ~ -200 V. The heavy and positive radicals/ions viz. C₂H₂, CH₃, CH₄, C₂H₄, C₂, and CH due to their low mobility, cannot be in phase with the RF power supply. However, due to the dc self-bias voltage on the target, make it possible the deposition of the film. Consequently, the magnitude of the bias on the substrate has an important effect on the formation of thin film. It also affects the film composition and properties of the films.
The frequency for the RF is 13.56 MHz and the original sine waveform output from the RF generator is shown in Figure 2.6. This AC voltage is applied onto the cathode through a capacitor between the cathode and the generator. After that the AC wavefunction will change from Figure 2.6 to Figure 2.7. In the first-half cycle, the cathode (substrate) is positive and
starts to accumulate electrons. During the next-half cycle the cathode is negative and begins
to collect positive ions from the plasma. The number of electrons collected in first half cycle
is very high compared to the number of positive ions collected in the rest half cycle. Because
of the higher mobility of the electrons ($>10^2$ times than that of positive ions), a net negative
charge accumulates on the target as there is a capacitor between the target and the RF
generator. The electrons collected on the target stay on the surface of the target for sometime.
In the first half of the second cycle, the fewer number of electrons will accumulate, as prior
gathered electrons still exist there. In the second half of the second cycle, the flux of positive
ions will be larger than that of the first cycle. After few cycles, the electron flux will be equal
to the ion current, and the system reaches the state of equilibrium. After equilibrium state,
most of the time the cathode voltage is negative, but remains positive for a short fraction of
time of each cycle. Therefore, Figure 2.7 shows that the target is effectively biased by a
negative dc potential with respect to ground. This bias enhanced nucleation (BEN) and bias
enhanced growth (BEG) methods are very crucial for growing NCD films with a steady self-
bias dc voltage (200-260 V) during the PECVD and MPCVD processes (in-situ nucleation
processes). The unique advantages of this technique are that it does not require any
pretreatment or pronunciation stage with the suitability of wide range of substrates. More
detailed discussion are given in introduction part of chapter 1.

2.3.3 Synthesis of Hydrogenated Diamond Like Carbon thin film onto

2.3.3.1 (a) Silicon (b) Quartz substrates

PECVD is used to deposit thin films from a gas state to a solid state on a substrate. Chemical
reactions are involved in the process, which occur after creation of plasma of reacting gases.
The plasma is generally created by RF (AC) frequency discharge between two electrodes, the
space between which is filled with the reacting gases.
The deposition process consists of two steps:

1. Etching of mirror polished Si(100)/quartz substrate of 10 mm diameter for 15 min. in a pure hydrogen ($H_2$ flow rate $\sim 500$ SCCM) plasma (light pink in color), at a pressure of 0.193 mbar, by 30 W RF forward power producing dc self-negative bias ($\sim -200$ V) with a impedance matching circuit, to remove any oxide layer from the surface of Si(100).

2. In situ Biased Enhanced Nucleation (BEN) process using helium (He flow rate $\sim 1500$ SCCM) plasma by 50 W RF power generating dc self-negative bias ($\sim -200$ V), with $H_2$ (flow rate $\sim 500$ SCCM) and $CH_4$ (flow rate $\sim 50$ SCCM) gases at a total pressure of 0.756 mbar and at substrate temperature $\sim 14 \, ^0C$, for 30 min. deposition time. The reactive unexploited gases are taken out from the deposition chamber during the deposition process and purged out to the environment after mixing with nitrogen gas.

**Experimental Parameters (Deposition Conditions) at a glance:**

1. RF : RF-Frequency 13.56 MHz;
2. RF-Power : 30 ± 2 Watt during etching process and 50 ± 2 Watt during deposition process.
3. Pressure : 0.20 ± 0.02 mbar during etching and 0.75 ± 0.05 mbar during deposition
4. Substrate : Si(100)/Quartz
5. Pre-treatment : By hydrogen plasma for 15 min. at 0.2 mbar
6. Gas Mixture : $CH_4$ (50 SCCM), $H_2$ (500 SCCM) and He (1500 SCCM) (SCCM - Standard Cubic Centimeter Per Minute)
7. Deposition time : 30 min.
8. Temperature : $14 \, ^0C$
2.3.3.2 Stainless steel

The stainless steel substrate (15 mm × 15 mm) was cleaned with NaOH followed by HNO₃ and then rinsed with millipore water. After cleaning, the argon ion sputtering was used to remove the passive chromium oxide layer for 15 minutes. The typical conditions used for sputtering were: flow rate of Ar gas 100 SCCM, total pressure 0.3 mbar, RF power 30 watts, dc self-bias –150 volts. After the sputtering, the steel surface was pre-treated with hydrogen plasma discharge. The typical conditions for this pre-treatment and deposition of HDLC over stainless steel substrate were tabulated in Table 2.1. Kumari et al. [91] have studied the HDLC coating over stainless steel using field effect and cross-sectional SEM (FESEM and XSEM) and energy dispersive X-ray analysis (EDX). They have reported the formation of a very smooth, continuous, non-porous, and homogeneous HDLC thin film coating with good adhesion properties. Therefore, I have not carried out any further study of HDLC film onto stainless steel substrate for my thesis work.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Silicon</td>
</tr>
<tr>
<td>RF Frequency (MHz)</td>
<td>13.56</td>
</tr>
<tr>
<td>RF Power (Watt)</td>
<td>30</td>
</tr>
<tr>
<td>Gases and Flow rate (SCCM)</td>
<td>H₂ (500)</td>
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<tr>
<td>Pressure (mbar)</td>
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<tr>
<td>Time (min.)</td>
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</tr>
<tr>
<td>Deposition</td>
<td>RF Power (Watt)</td>
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<tr>
<td>Bias (V)</td>
<td>-200</td>
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<tr>
<td>---</td>
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</tr>
<tr>
<td>Pressure (mbar)</td>
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<tr>
<td>Time (min.)</td>
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<tr>
<td>Gases and flow rate (SCCM)</td>
<td>He (1500), H₂ (500), CH₄ (50)</td>
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<tr>
<td>Temp (°C)</td>
<td>14</td>
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<tr>
<td>Nitrogen Flow (SCCM)</td>
<td>500</td>
</tr>
</tbody>
</table>

*Sputtering condition: RF power 30 watts, dc self bias 150 volts, total pressure 0.3 mbar, time 15 min.*
Figure 2.8 Picture of the film (golden color) deposited by PECVD method on 10 mm dia mirror polished silicon substrate

Figure 2.9 Pictures of the films (yellow color) deposited by PECVD method on 25 mm×25 mm quartz substrate
2.3.4 Description of the major parts of the System

**Cathode**: 250 mm dia. of metallic electrode connected to the RF matching circuit and power supply

**Anode**: Aluminum walled body connected to the ground as a anode and always at zero potential. Each wall side of the body is 50 cm × 50 cm.

**RF-Matching Circuit**: Contains an induction and capacitance circuit for matching the impedance between the input (RF circuit) and output (Plasma) systems

**Vacuum pumps**:

(a) Mechanical pump is switched on for making the chamber pressure from atmospheric to ~ 0.1 mbar. Small traces of oil are absorbed by the chemical filter which prevents the contamination during the processes of deposition.

(b) Roots pump is switched on when the pressure is ~0.1 mbar and continued until the pressure reaches desired value (~$10^{-4}$ mbar)

**Closed loop cooled water circulation system**: Cooling of the substrate and cathode using a cooler maintained at $10^0$C.
2.4 Annealing of HDLC samples

A few number of HDLC samples were prepared by PECVD method by varying the flow rate of methane 20, 30, 40, 50, 70, and 90 SCCM. Few sets of such HDLC samples were heated at a fixed temperature of 100, 250, 750, 900, and 1050 °C for 30 minutes in high vacuum ~1×10⁻⁶ torr and cooled to room temperature after heating in one set of experiment. The as prepared and annealed HDLC sample at 1050 °C were analyzed using confocal micro Raman spectra, current-voltage characteristics in ambient air, topographic image of the sample using AFM, and STM measurements under constant tunneling current mode. The results and discussion based upon the above measurements are given in chapter 4. The annealing experiments were carried out in Bioceramic and Coating Division, in CSIR-Centre of Glass and Ceramic Research Institute, Kolkata, India. The pictures of the HINDHIVAC instrument for annealing of HDLC samples at high temperature and high vacuum are shown below.

**HINDHIVAC Instrument**

**Instrument Controller**

**Controlled Parameters at a glance**

1) Temperature : 100 °C to 1050 °C (maximum)

2) Pressure : 1 × 10⁻⁶ torr

3) Annealing time : 30 minutes (for all samples)

4) Heating rate : 5 °C/min.

5) Cooling rate : 3 °C/min.
Figure 2.10 HINDHIVAC vacuum and sample heating control unit
Figure 2.11 HINDHIVAC Vacuum sample heating chamber
2.5 HDLC samples preparation for IBA study

Another few sets of samples were prepared by PECVD method at flow rate of methane 20, 30, 40, and 70 SCCM, by varying CH$_4$ to H$_2$ ratio at room temperature. One such set of samples was heated at a heating rate 5 °C/min under vacuum ($1 \times 10^{-7}$ torr) at temperature 750 °C and 1050 °C. These films are kept in the above desired target temperature for 30 minutes before cooling them to room temperature at a cooling rate of 3 °C/min. The as-prepared and annealed HDLC films have been depth profiled for hydrogen using the nuclear resonance at 6.44 MeV in $^1H(^{19}F,\alpha\gamma)^{16}O$ nuclear reaction by heavy ion beam. The Rutherford backscattering (RBS) on the as-prepared and annealed samples, with 1.0 MeV proton ion beam is carried out to measure the thickness of HDLC films. Both NRA and RBS measurements are carried out by a 3 MV Tandetron accelerator at the surface and profile measurement laboratory of the National Center for Compositional Characterization of Materials (NCCCM), Hyderabad, India. The results and discussion based upon the above measurement are given in chapter 4 (section 3). The picture of the NRA/RBS measurement instrument for depth profiling HDLC samples is shown below.
Figure 2.12 Picture of experimental arrangement for IBA study