

Chapter 2

Multi-Chamber CVD System and Cu Precursor

2.1 Multi-Chamber Cu CVD System

A multi-chamber low pressure chemical vapor deposition (CVD) system with a warm wall reaction chamber built in our laboratory is used for this thesis study. Figure 2-1 shows the schematic diagram of this multi-chamber CVD system, the photographs of which are illustrated in Fig.2-2 and Fig.2-3. There are four chambers in the CVD system: (1) loading chamber, (2) transfer chamber, (3) plasma pre-treatment chamber, and (4) reaction chamber. Moreover, the CVD apparatus also contains a direct liquid injection (DLI) and a catalyst injection system. The details of each chamber and sub-system are described as follows.

[1] Loading Chamber

The loading chamber is a buffer between the controlled vacuum environment inside the CVD system and the atmospheric environment outside the system. The function of this chamber is to handle the substrate input and output. The substrate wafer is placed on an Al made substrate holder; either a whole piece of wafer up to an 8-inch diameter or broken pieces of wafer can be placed on the substrate holder. The substrate wafer (together with the substrate holder) can be transferred to any desired chamber via a robot arm that is set in the transfer chamber.

[2] Transfer Chamber

This is a hexagonal shaped chamber directly connected to each of the other chambers of this multi-chamber CVD system. The transfer chamber houses a robot arm, the function of which is to carry the substrate holder and transfer it to the designated chamber. The operation

of the robot arm is controlled and monitored by a robot controller via a host computer system. Figure 2-4 is a photograph showing the robot arm in the transfer chamber.

[3] Pretreatment Chamber

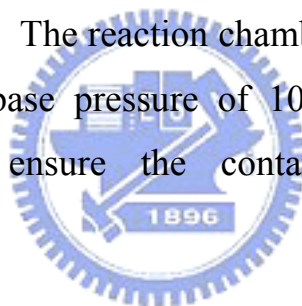
Prior to the deposition of copper films, the substrate wafers may be pretreated by plasma in this chamber. Figure 2-5 shows the schematic diagram of the pre-treatment chamber. The chamber wall is grounded, and a 600W power generator operated at a radio frequency of 13.56 MHz is used for the plasma generation. The plasma can be induced in the pretreatment chamber by a negative DC bias [21]. Various gases, including Ar, N₂ and H₂, can be introduced into the chamber for the generation of different plasma [22, 23]. The plasma treatment on the substrate surface can be classified into two different types: physical sputtering treatment (such as Ar-plasma) and chemical reaction treatment (e.g. H₂-plasma).

For the physical sputtering treatment in Ar-plasma, the ionized Ar ions are accelerated to bombard the substrate surface, resulting in the removal of native oxide and organic contamination from the substrate surface. On the other hand, the H₂-plasma treatment is mainly a chemical reaction process because the ionized hydrogen radical tends to chemically react with the surface materials to produce volatile reactants, which can be easily removed from the chamber.

The most advantage of multi-chamber CVD system is that the pretreated substrate wafer can be directly transferred to the reaction chamber for Cu film deposition without breaking the vacuum. Thus, any possible contamination by the atmospheric environment can be avoided.

[4] Reaction Chamber

This is the chamber where the reaction of precursor is to take place for the deposition of Cu films. Figure 2-6 shows a schematic diagram of the reaction chamber. On the top of the chamber there is a shower-head injector, through which the Cu precursor carried by the carrier gas is delivered into the reaction chamber. Under the injector there is a substrate holder, which can be heated by a resistive heating element. The substrate holder is rotatable so as to obtain a better uniformity of the deposited Cu films. It can also be moved in vertical direction so that the distance between the injector and the substrate can be adjusted. The sidewall of the cylindrical reaction chamber as well as the Cu precursor injector is kept at a temperature of 45°C by circulating warming water to prevent Cu precipitation. The reaction chamber of this CVD system can be pumped down to a base pressure of 10^{-7} torr before the Cu films deposition process to ensure the contamination free deposition environment.



[5] Direct Liquid Injection (DLI) Delivery System of Precursor

The liquid Cu precursor is delivered by a direct liquid injection (DLI) system which is composed of a liquid flow controller (LFC) and a controlled evaporation mixer (CEM). A schematic diagram of the DLI system is illustrated in Fig.2-7. The liquid precursor is propelled by the nitrogen gas through the LFC which can precisely control the mass flow of the liquid precursor. The precursor is then vaporized in the CEM unit and mixed with the carrier gas. Finally, the carrier gas with its carried precursor is directed into the reaction chamber through the gas injector.

[6] Catalyst Storage and Injection System

Liquid C_2H_5I was used in this study to provide iodine (I_2) as catalyst

for the CVD of Cu films. C_2H_5I has a high vapor pressure of 137.52mmHg at 25°C. In this study, the container of the liquid C_2H_5I was kept at a constant temperature of 25°C, and a mass-flow controller (MFC) is connected to the container through a valve, as shown schematically in Fig.2-8. When the valve is opened, the iodine containing vapor will enter the reaction chamber by diffusion. The parameters of the mass-flow controller are set ready at the beginning and the vapor flow is totally controlled by the valve.

2.2 Automatic Monitor and Controller System

Figure 2-9 shows the automatic remote monitor and controller (ARMC) system for the multi-chamber Cu-CVD system. The design concept of this automatic controlling system is focused on the requirements of gas transport, vacuum procedure sequences controlling, substrate plasma treatment, substrate heating control, pressure control, safety protection handling, users friendly interface, and convenient maintenance.

The ARMC system is composed of a host computer, a subsidiary controller, and a unit controller of the Cu CVD apparatus. A communication program is designed to link together the functions of the host computer and the subsidiary controller. Therefore, data and commands can be transferred between them through a dynamic data exchange (DDE) server in Windows-98 operation system. In the host computer, a friendly interface program with monitor and control function is operated under the Windows-98 operation system, as shown in Fig. 2-10. The deposition process and the procedure sequences are under automatic control by this friendly interface program. What the user needs to do is to program the recipes and process steps correctly and precisely, and the host computer will monitor all of the operation

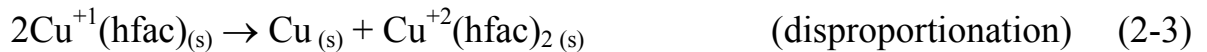
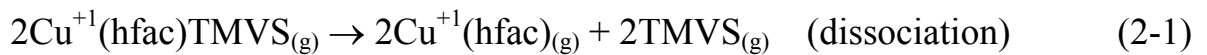
conditions of the Cu CVD system.

2.3 Reaction of Cu Precursor

The precursor used in this thesis study is a liquid Cu(I) precursor of Cu(1,1,1,5,5,5-hexafluoroacetylacetonate)trimethylvinylsilane plus 2.4wt%TMVS developed by Schumacher company [2, 23]. The 2.4wt%TMVS additive promotes stability of the precursor.

The Cu^I(β-diketonates) is one of the most promising Cu precursors [24]. The Cu(I) precursors have a form of Cu^I(β-diketonates)L, where L is a neutral ligand weakly bonded to Cu. Hexafluoroacetylacetonate (hfac) is the most commonly used β-diketonates. The structure of Cu^I(hfac)L is similar to that of Cu^{II}(hfac)₂, with the L ligand replacing one of the hfac rings. Depending on the L ligand, CVD of Cu films may have a selective deposition property. Low resistivity Cu films can be deposited from Cu^I(hfac)TMVS at temperatures below 200°C.

It has been proposed that the complete disproportionation reaction of the Cu^I(hfac)TMVS precursor consists of four steps as follows [23]



where (g) denotes “gas phase” and (s) denotes “adsorbed on substrate surface.” The first step involves the decomposition of Cu(hfac)TMVS into Cu⁺¹(hfac) and TMVS species by the gas phase reaction (Eq.2-1); this is because Cu-TMVS in the Cu(hfac)TMVS precursor is a weak bond

compared to the Cu-hfac bond. This is followed by the adsorption of the $\text{Cu}^{+1}(\text{hfac})$ species on the substrate surface (Eq.2-2). The $\text{Cu}^{+1}(\text{hfac})$ species then undergo a disproportionation reaction to produce the Cu metal and the Cu(II) species $[\text{Cu}^{+2}(\text{hfac})_2]$ (Eq.2-3). Finally, the volatile $\text{Cu}^{+2}(\text{hfac})_2$ by-product desorbs from the substrate surface (Eq.2-4). The reaction step 3 (Eq.2-3) is the key step of Cu nucleation on the substrate surface, which involves a process of electron exchange between the adsorbed $\text{Cu}^{+1}(\text{hfac})$ and the substrate surface. Thus, it is easier to deposit Cu film on a conducting substrate than an insulating substrate. The overall reaction of Cu film deposition is given by the equation as follows:

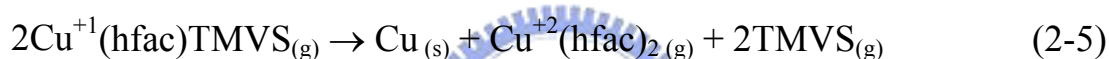


Figure 2-11 illustrates the four steps of Cu film deposition by $\text{Cu}(\text{hfac})\text{TMVS}$ precursor.

It was reported that the bond breaking temperature for $\text{Cu}^{(I)}\text{-TMVS}$ was approximately 63°C , and that as the dissociation temperature of $\text{Cu}^{(I)}\text{-L}$ increases, the copper precursor becomes more thermally stable [25]. The volatility of TMVS is very high, and complete TMVS desorption from the surface occurs around 398-423 K ($125\text{-}150^\circ\text{C}$). It is believed that the $\text{Cu}^{+2}(\text{hfac})_2$ is the major contributor of the impurity contamination.

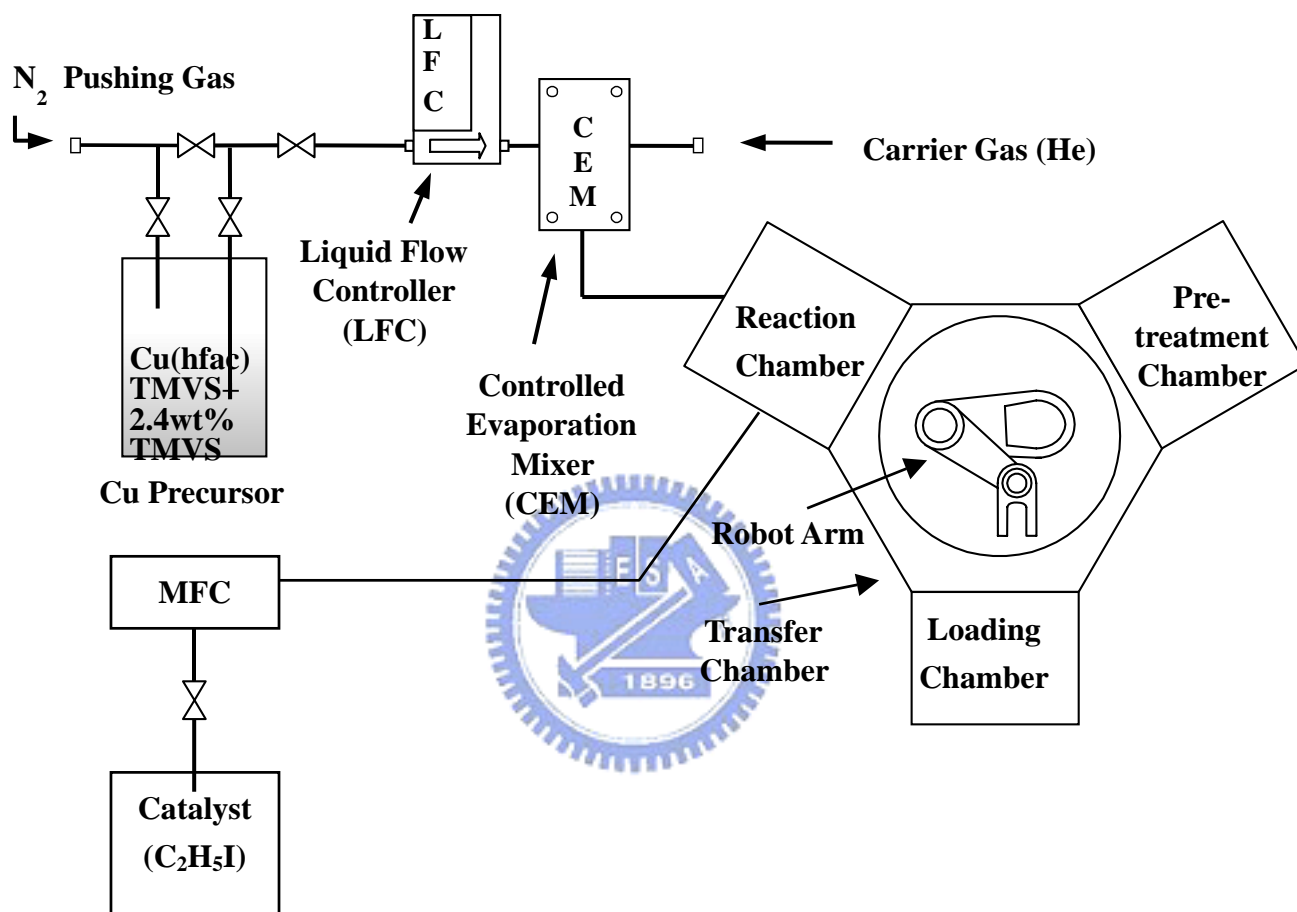


Fig.2-1 Schematic diagram of multi-chamber Cu CVD system used in this thesis study.

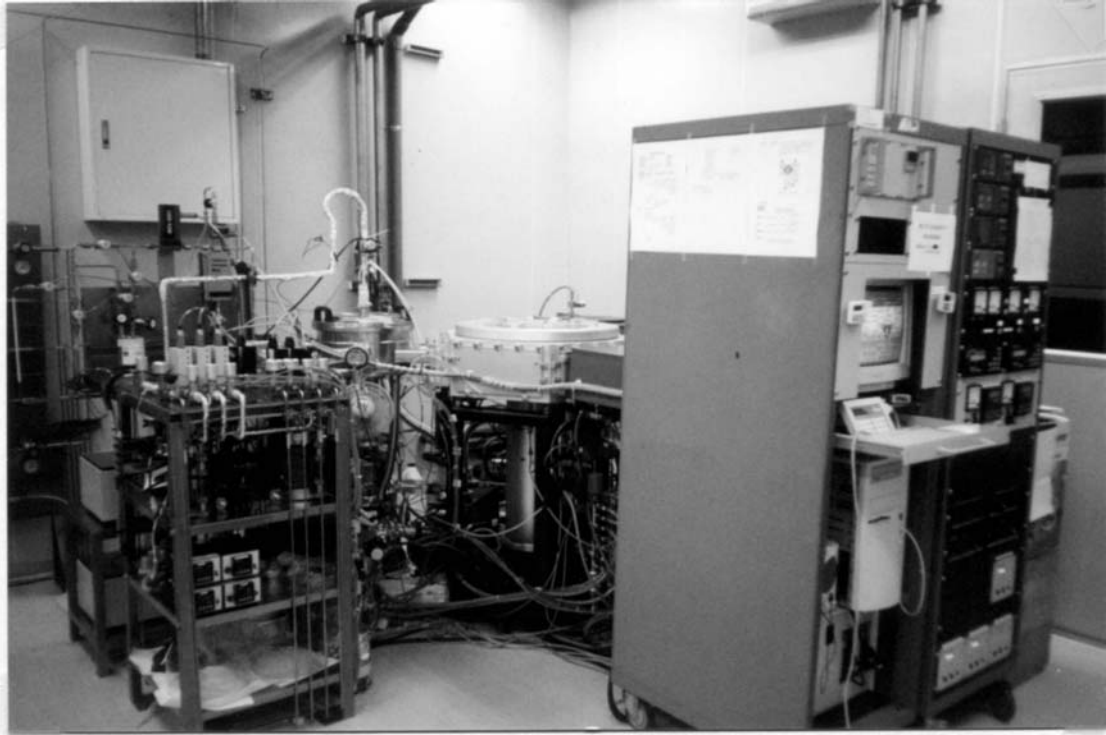


Fig.2-2 The panorama photograph of the multi-chamber Cu CVD apparatus.

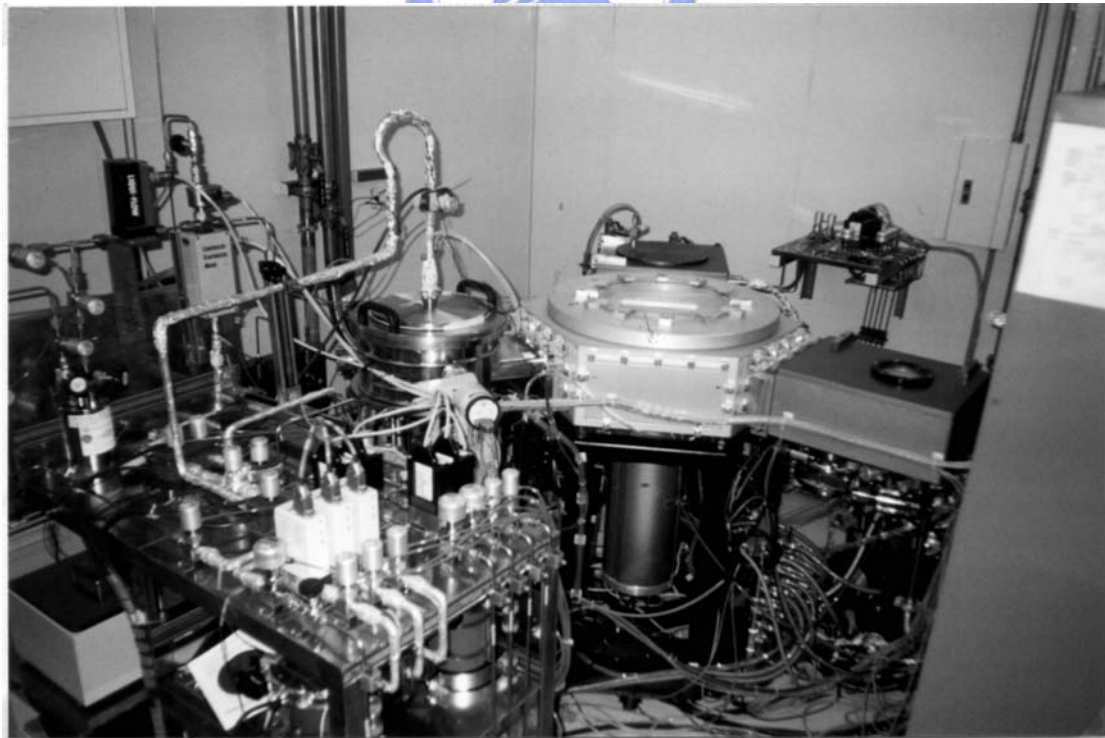


Fig.2-3 Photograph showing the cluster-chamber, DLI system, and gas piping system.



Fig.2-4 Photograph showing the robot arm in the transfer chamber.

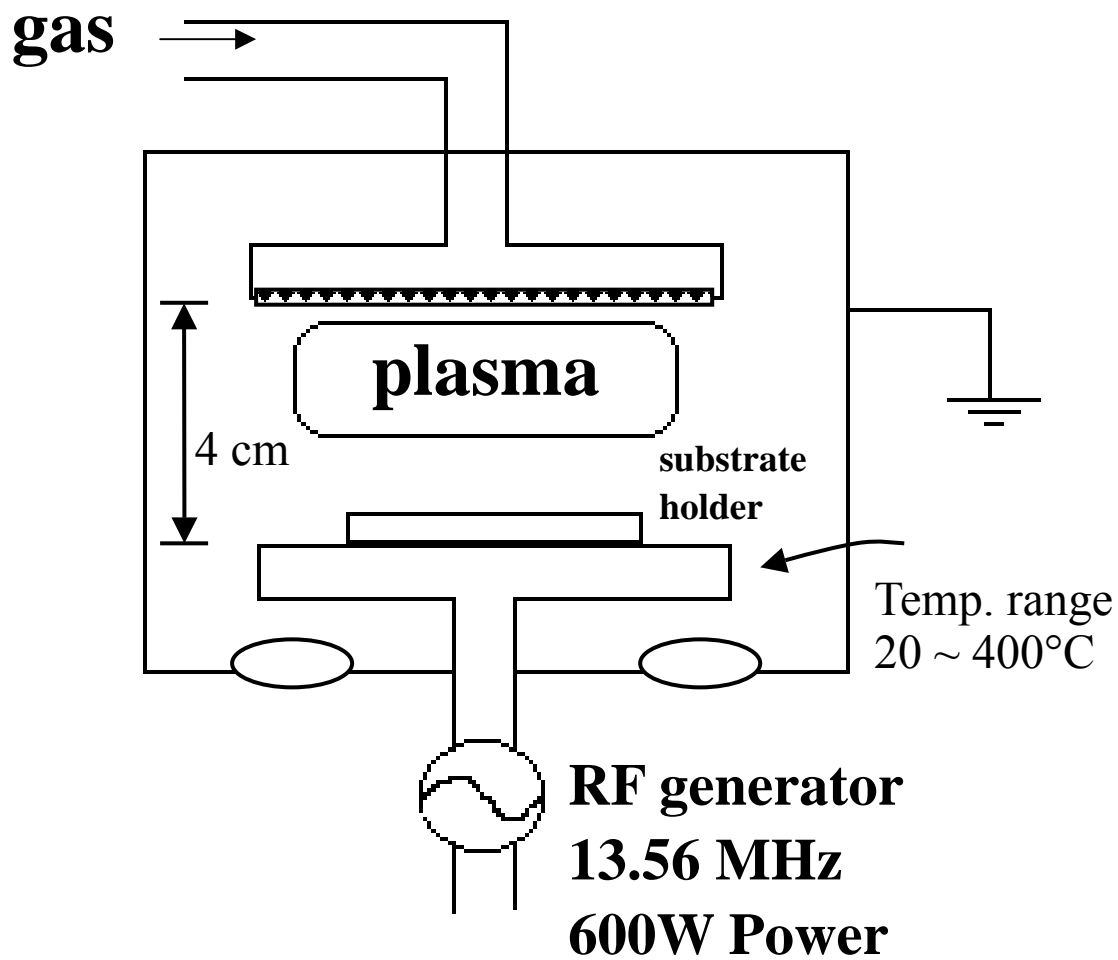


Fig.2-5 Schematic diagram of the pretreatment chamber.

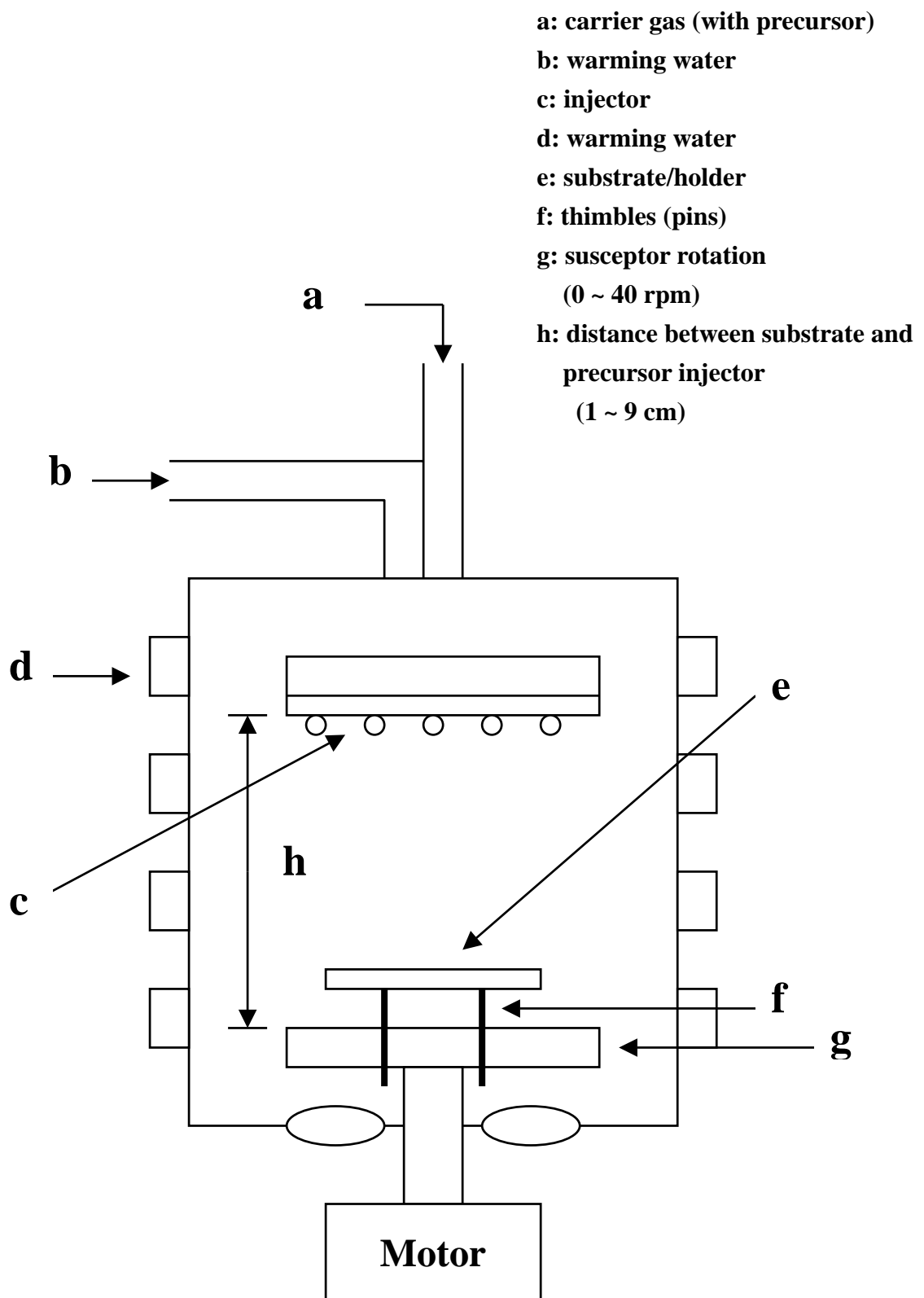


Fig.2-6 Schematic diagram of the reaction chamber (copper deposition chamber) and gas injector.

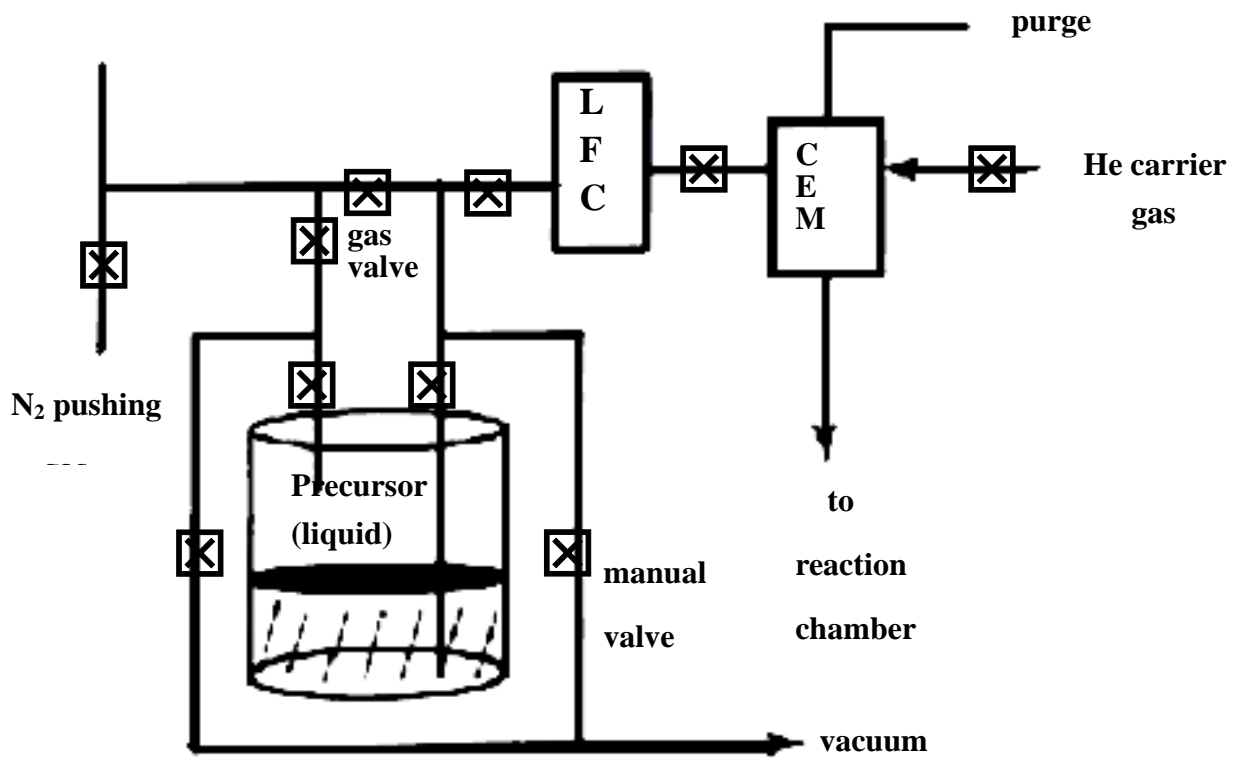


Fig.2-7 Schematic diagram of direct liquid injection (DLI) precursor delivery system.

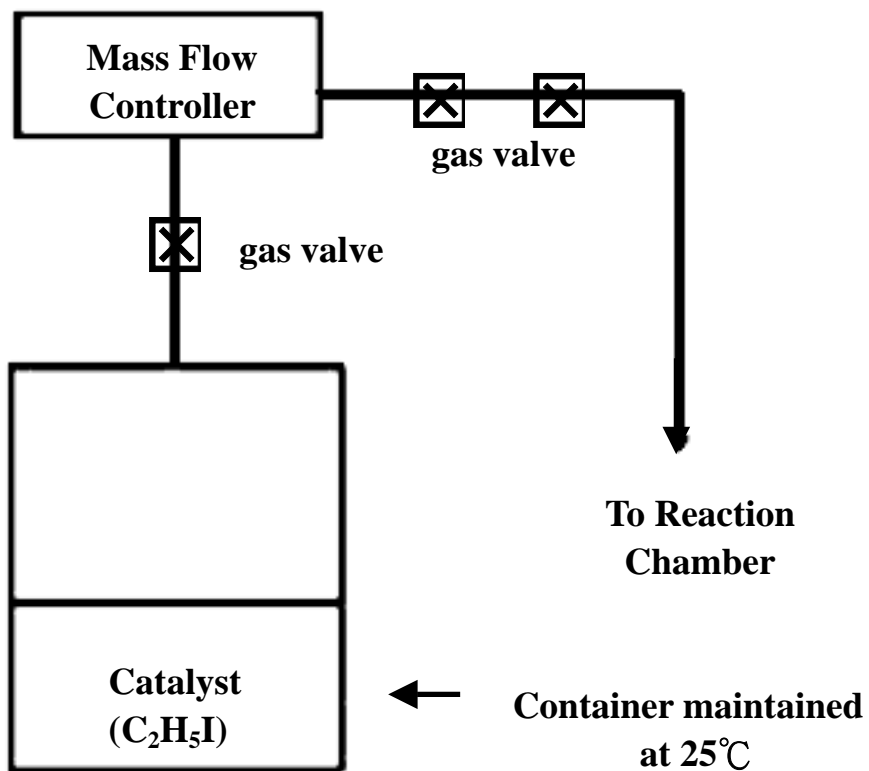
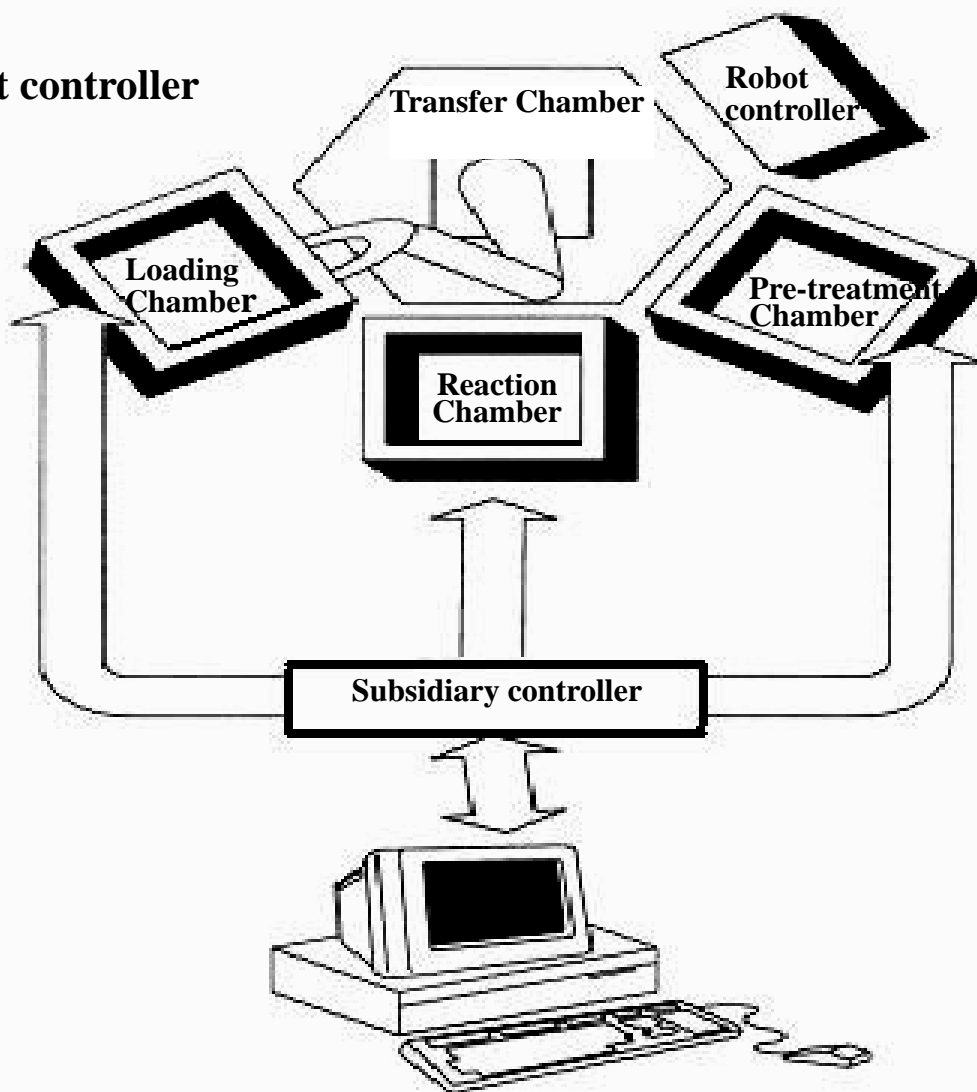


Fig.2-8 Schematic diagram of catalyst storage and injection system

Unit controller



Host Computer

Fig.2-9 Schematic diagram of automatic remote monitor and controller system, which is composed of a host computer, a subsidiary controller, and unit controller of the Cu CVD apparatus.

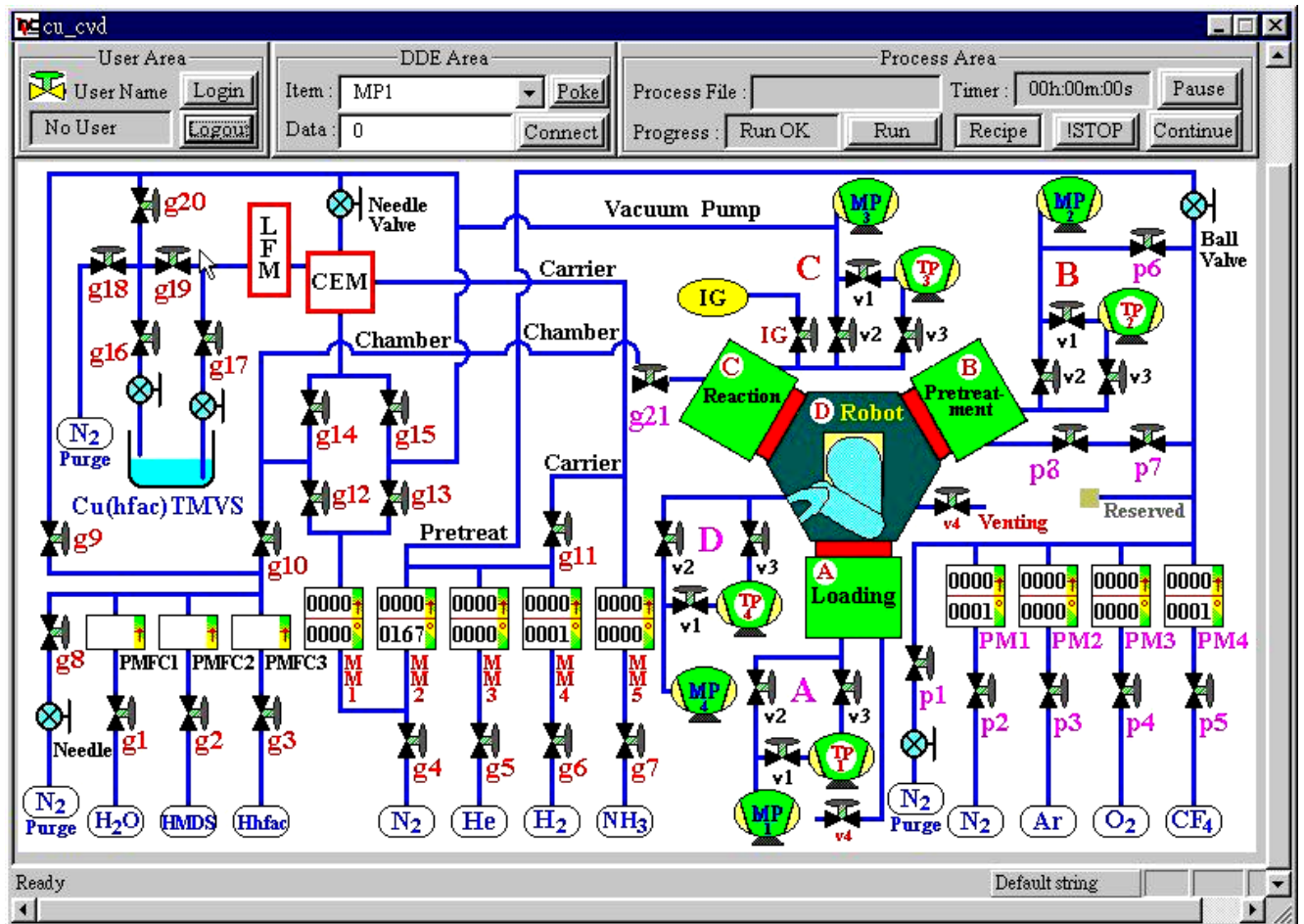


Fig.2-10 The friendly monitor and control program displays in the host computer screen.

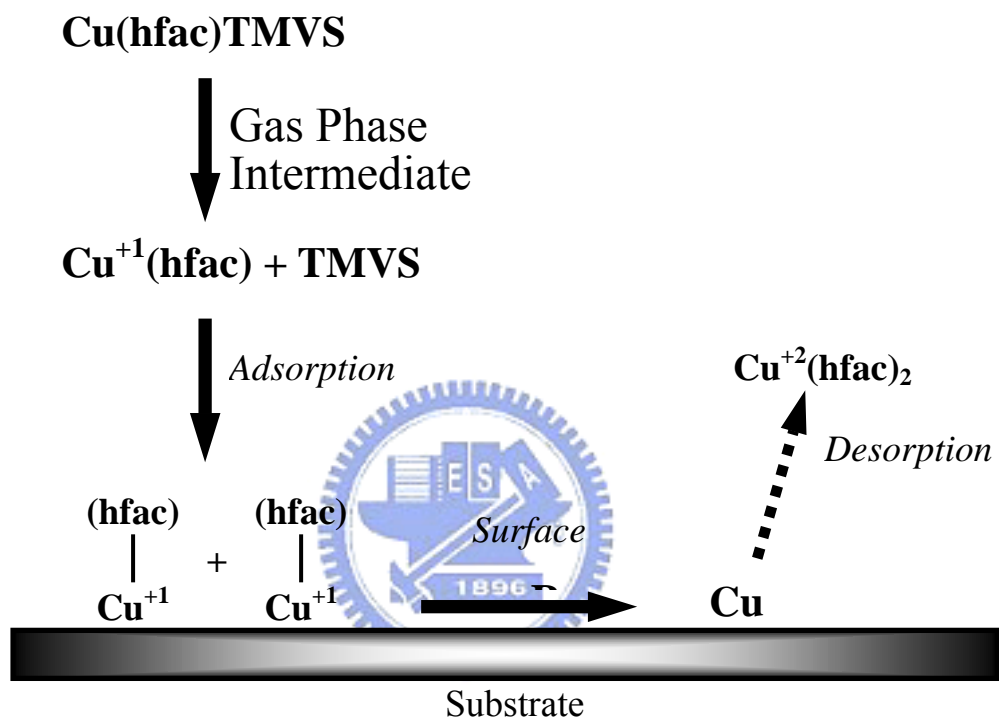


Fig.2-11 The deposition mechanism of Cu CVD by Cu(hfac)TMVS precursor.