Plasma Enhanced Liquid Source MOCVD System

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Abstract. Plasma enhanced liquid source MOCVD system was developed in Xi’an Technological University. The system was developed for the deposition of complex oxide thin films for electronic and photo-electronic applications. Liquid source delivery method was adapted to enable the application of metal-organic precursors with low vapor pressure in the MOCVD procedure. The system can be used for the deposition of complex oxide ferroelectric thin films such as Pb(Zr,Ti)O$_3$ and (Ba,Sr)TiO$_3$.

1. Introduction
Complex oxide thin films, especially perovskite oxides have important applications in electronics and photo-electronics, such as ferroelectrics and high temperature superconductors. MOCVD is among the top list of the deposition methods for the preparation of the thin films. In conventional MOCVD method, metal organic (MO) precursors with high vapor pressure are required. To vaporize the MO precursors, bubblers are usually used. But for complex oxide thin film deposition, the difficulty is that the precursors to be used have large difference in their vapor pressure. In some cases, the precursor used has so low vapor pressure that the MOCVD process is impractical. To deliver liquid source with low vapor pressure, different methods such as misted sol-gel and high pressure nozzle injection were used [1, 2, 3].

Objectives of this research are to adapt a new method for the vaporization of MO precursors with low vapor pressure and to enhance the deposition procedure with radio frequency plasma. In this paper, the configuration of a newly developed MOCVD system is described in details, the preliminary application of the system is presented.

2. System configuration
Plasma enhanced liquid source MOCVD system is proposed as shown in figure 1.

The system is composed of a closed-loop pressure control vacuum sub-system, a plasma generation and chemical reaction chamber, a liquid source metering, feeding and vaporization sub-system, temperature control modules and gas flow control sub-system. The working flow of the system can be described as that in figure 2.
2.1. Liquid delivery and vaporization
Figure 3 shows the liquid delivery sub-system. A gas tight reservoir is used for the storage of the liquid precursor. The gas absorbed in the liquid source is removed through the degas port by applying a negative pressure. The high precision piston pump and the backpressure valve are used as the liquid feeding and metering components.

The vapor of the liquid precursor is generated by using a 120 kHz ultrasonic atomizer combined with a temperature controlled mixing chamber, where the vapour is mixed with the carrying gas and the reaction gas. The vaporizer shown in figure 4 can be applied for the vaporization of MO precursors with low vapor pressure.

2.2. The reaction chamber and the pressure control
Vaporized precursor is fed into the reaction chamber as shown in figure 5. The shower head for the uniform distribution of the vapor is temperature controlled and operated as the anode of the RF discharge system. The plasma generated in the reaction chamber is sustained with an auto-matched
300W 13.56 MHz RF power source. The substrate for the deposition of the thin films can be heated to 650°C by the heater.

To control the background pressure and the working pressure of the MOCVD deposition process, a closed-loop pressure control sub-system is built as in figure 6. By selecting appropriate membrane gauge, the pressure can be precisely controlled in the range of 1~1000Pa or 10~10000Pa through the actuation of the throttle valve.

2.3. System specifications
Specifications achieved for the system are listed in table 1.

| Parameter                      | Specification                  |
|--------------------------------|--------------------------------|
| Liquid delivery rate           | 0~10 ± 0.01 ml/hr.             |
| Carrying gas flow rate         | 0-1000 ± 10 SCCM               |
| Substrate temperature          | RT~650°C                       |
| Vaporizer temperature          | RT~350°C                       |
| Gas temperature                | RT~350°C                       |
| Shower head temperature        | RT~350°C                       |
| Pressure                       | 1~1000Pa or 10~10000Pa         |
| Pumping speed                  | 150m³/hr                       |
| RF power                       | 13.56MHz, 0~300W, Auto Match   |

3. System application
The system can be used for the deposition of complex oxide ferroelectric thin films such as Pb(Zr,Ti)O₃(PZT) and (Ba,Sr)TiO₃(BST). To demonstrate the application of the system, preliminary results on the preparation of PZT thin films are reported hereafter.

Precursor of the PZT was prepared as described elsewhere[4]. The precursor has a concentration of 0.1M. Parameters used for the deposition of the PZT thin films are listed in table 2.
Table 2 PZT thin film deposition parameters

| Parameter                      | Value          |
|-------------------------------|---------------|
| Liquid Flow Rate              | 0.1 ml/min    |
| Oxygen/Argon Flow Rate        | 500/300 SCCM  |
| Chamber Pressure              | 800 Pa        |
| RF Power                      | 50 W          |
| Substrate Temperature         | 550 °C        |
| Gas Temperature               | 130 °C        |
| Shower Head Temperature       | 130 °C        |
| Vaporizer Temperature         | 130 °C        |

The PZT thin films were deposited onto silicon wafer with Pt/Ti/SiO$_2$ electrode and buffer layers. The thickness of the deposited PZT thin film was measured by using an interferometer. For a 150nm PZT thin film, the deposition time was 15 minutes.

XRD pattern of the thin film with a thickness of 150nm as shown in figure 7 proves that the PZT thin film deposited has pure perovskite phase.

4. Conclusions
Plasma enhanced MOCVD system for the deposition of complex oxide thin films was successfully developed. Ultrasonic atomizer together with liquid flow metering and feeding method was applied to deliver MO precursor with low vapor pressure, which makes the MOCVD system more feasible to the deposition of complex oxide thin films. Plasma was introduced into the deposition procedure to enhance the chemical reactions.

Further investigations on the properties and applications of the complex oxide thin films deposited by using the developed system are undergoing.

References
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