Characterization of inductively coupled RF plasmas for plasma-assisted mist CVD of ZnO films

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Abstract. A plasma-assisted mist chemical vapor deposition (CVD) system with a high-density inductivity coupled RF plasma (ICP) source has been developed for low-temperature and high-rate deposition of zinc oxide films. In this paper, characterization of an ICP for plasma-assisted mist CVD is reported. It was found that the plasma density measured with a cylindrical Langmuir probe was as high as $1.2 \times 10^{11} \text{ cm}^{-3}$ and the electron temperature was 1.0 - 2.5 eV for an Ar plasma. The gas temperature in the ICP determined from molecular optical emission spectroscopy was 1450 K at an RF power of 1000 W for an Ar/air plasma. These results demonstrate that a plasma sustained by an inductively coupled RF plasma source has sufficient enthalpy for vaporization of mists and also has a high density for efficient dissociation of precursors and generation of oxygen radicals during ZnO film deposition using plasma-assisted mist CVD.

1. Introduction
In recent years, zinc oxide (ZnO) has attracted considerable attention due to its diversity of applications. ZnO is a wide band semiconductor with a direct band gap of 3.37 eV at room temperature, which makes it a possible candidate for optical and electrical devices, such as ultraviolet emitters and detectors, transparent conductive oxides (TCOs), heterojunction transistors, thin film transistors and sensors [1-3]. For application to transparent conducting electrodes, the high electrical conductivity, high transparency to visible light, and material abundance make ZnO a very promising alternative to tin-doped indium oxide (ITO). Deposition of high-quality ZnO films for TCOs is attracting attention as one of the key technologies for fabrication of silicon thin-film solar cells to produce low-carbon energy. ZnO thin films have been deposited using various methods including dry processes such as magnetron sputtering [4-7], reactive evaporation [8], pulsed laser deposition (PLD) [9,10], metal organic chemical vapor deposition (MOCVD) [11,12], molecular beam epitaxy (MBE) [13,14], and wet processes such as spray pyrolysis [15-17], sol-gel [18] and mist CVD [19-21]. The dry deposition techniques are suitable for obtaining high-quality crystalline thin films; however, the deposition rate is low compared with that of wet processes. While wet deposition techniques contribute to system simplicity and high-rate deposition, the controllability of these processes is generally worse than that of dry processes. Furthermore, substrate heating is essential for pyrolysis in wet processes. Therefore it is difficult for conventional wet processes to deposit ZnO films on polymer materials since polymer materials are heat-sensitive.

In order to address these problems, we have developed a plasma-assisted mist CVD method that uses a high-density inductively-coupled RF plasma source, allowing low-temperature and high-rate...
Plasma-assisted mist CVD is a combination of mist CVD [19-21], which has the advantages of treating mist particles like gas, and plasma-assisted deposition. In this method, a water and/or alcohol solution of a metallic salt of zinc is ultrasonically atomized to form mist particles of the solution, and the particles are then transferred by a carrier gas onto the substrate, forming a ZnO film promoted by chemical reactions due to plasma irradiation. It is possible for this method to control both surface reactions and chemical reactions in the gas phase, allowing low-temperature and high-rate deposition of ZnO films.

We consider that in plasma-assisted mist CVD, the gas temperature together with the plasma density are among the key parameters determining the properties of the deposited films since they influence vaporization of the mists, gas-phase reactions of radicals and surface reactions of the precursors.

In this study, characterization of inductively coupled RF plasmas for plasma-assisted mist CVD was carried out in terms of plasma density and gas temperature.

2. Experimental

A schematic diagram of the experimental setup for the plasma-assisted mist CVD reactor is shown in Fig. 1. A water-cooled copper coil antenna (three turns) is looped around an alumina discharge tube with an outer diameter of 50 mm and an inner diameter of 42 mm. The antenna is coupled to a 1000 W RF power generator at 13.56 MHz via a matching network. Ar and Ar/air mixture gases are supplied at a flow rate of 2.5 slm and 2.5 slm/12.5 sccm, respectively, from upstream of a stainless tube with an outer diameter of 18 mm and an inner diameter of 15 mm. In the actual deposition process, a Zn(CH3COO)2 solution was used as the zinc oxide source. The Zn(CH3COO)2 solution was used as the zinc oxide source. The Zn(CH3COO)2 solution was supplied by ejection of droplets of Zn(CH3COO)2 solution from a nozzle in the vacuum chamber. The total pressure was kept constant at 10-100 Pa. The Si and glass substrates were located in the downstream region at 300 mm from the copper coil antenna.

The plasma density and electron temperature were measured with a cylindrical Langmuir probe at a distance of 195 mm from the antenna. Optical emission spectroscopy (OES) analysis was carried out using a high-resolution fiber optic spectrometer (Ocean Optics HR-4000).

3. Theoretical background for spectral analysis

In this study, we analyzed the first and second positive systems of a nitrogen molecule to estimate the vibrational and rotational temperatures. Generally, the line intensity of the radiative transition of a molecule \((n', v', J') \rightarrow (n'', v'', J'')\), where \(n\) is the electronic state, \(v\) is the vibrational quantum number and \(J\) is the rotational quantum number, can be expressed as

\[
I(n', v', J' \rightarrow n'', v'', J'') = h\nu A(n', v', J' \rightarrow n'', v'', J'')N_{n', v', J'}
\]  

(1)
where \( I(n', v', J' \rightarrow n'', v'', J'') \) is the radiant flux of the emission, \( h \) is Planck's constant and \( N_{n', v', J'} \) is the number density of molecules in the upper states.

Concerning the transition probability \( A(n', v', J' \rightarrow n'', v'', J'') \), we have \[ A = \frac{64\pi \nu^3}{3\hbar c^3\gamma_{n'v'}^2} \sum J'f' |\tilde{R}_{J'f'}|^2 q_{n'v'} S_{J'}, \] (2)

where \( c \) is the velocity of light, \( \sum J'f' |\tilde{R}_{J'f'}|^2 \) is the transition moment, \( g_{n'} \) is the statistical weight of the electronic state \( n' \), \( q_{n'v'} \) is the Franck–Condon factor and \( S_{J'} \) is the HönL–London factor.

When we assume a Boltzmann distribution for the vibrational and rotational states, the number density of molecules in the upper states \( N_{n', v', J'} \) is rewritten as

\[
N_{n', v', J'} = N_n \exp\left(-\frac{E_{vib}}{kT_{vib}}\right)(2J'+1)\exp\left(-\frac{E_{rot}}{kT_{rot}}\right),
\] (3)

where \( N_n \) is a constant independent of \( v \) and \( J \), \( k \) is the Boltzmann constant, \( T_{vib} \) and \( T_{rot} \) are the vibrational and rotational temperatures, respectively, and \( E_{vib} \) and \( E_{rot} \) are the vibrational and rotational energy levels, respectively.

Considering the above equations, we can describe the unique rotation-vibration spectrum as a function of vibrational and rotational temperatures. Therefore, we can determine these temperatures by fitting the calculated spectrum to that measured experimentally.

In this study, we used the second positive system (2ndPS) bands for the estimation of the gas temperature. The 2ndPS appear frequently in ordinary discharges. This system corresponds to a transition between the electronic states \( C^3\Pi_u \) and \( B^3\Pi_g \).

To calculate the spectrum of the 2ndPS, we neglected the spin splitting; the line strengths for the \( P \), \( Q \), and \( R \) branches are combined. Therefore, we considered three rotational transitions and two vibrational transitions, namely, \((v', v'') = (0, 2) \) and \((1, 3) \).

The transition probability in the second positive system \( A_{\frac{C}{B}v'J'} \) is written as

\[
A_{\frac{C}{B}v'J'} = A_{\frac{C}{B}v'} \frac{S_J}{6(2J'+1)},
\] (4)

where \( S_J \) for the \( P \), \( Q \), and \( R \) branches is given as \[ P(J + 1) = 6(J + 1) - 10/(J + 1), \] (5) \[ Q(J) = 10/J + 10/(J + 1), \] (6) \[ R(J - 1) = 6J - 10/J. \] (7)

\textbf{4. Results}

To investigate the characteristics of the plasma source for plasma-assisted mist CVD of ZnO films, the plasma density and electron temperature for argon gas (Ar 100\%) at a distance of 195 mm from the
antenna were measured. Figure 2 shows the plasma density and electron temperature of plasma sustained by an inductively coupled plasma source for plasma-assisted mist CVD. The plasma density and electron temperature became as high as $10^{11}$ cm$^{-3}$ and 1.0 - 2.5 eV at a distance of 195 mm from the antenna. This result indicates that an inductively coupled plasma source can generate a high-density plasma for efficient deposition of ZnO films using plasma-assisted mist CVD.

To measure the gas temperature, we introduced an air-in-Ar plasma and performed optical emission spectroscopy measurements of the N$_2$ second positive system. Figure 3 shows a typical optical emission spectrum in the range of 300 - 900 nm for an Ar/air plasma sustained at an RF power of 1000 W. The optical emission spectrum contains electronic spectral lines of the first positive system (B$^3\Pi_u$ and A$^3\Sigma^+_g$) and the second positive system (C$^3\Pi_u$ and B$^3\Pi_u$). As shown in Fig. 4, the optical emission spectrum in the range of 700 - 900 nm contains atomic spectral lines from the oxygen radials that contribute to oxidation of ZnO films and removal of the organic impurities attributed to precursors. Figure 5 shows the spectrum of the N$_2$ second positive system for $\nu' - \nu'' = \Delta \nu = -2$. In this study, to determine the vibration and rotational temperature, we used the electronic spectrum of the second positive system (C$^3\Pi_u$ and B$^3\Pi_u$) in the range of 370 - 385 nm. Figure 6 shows comparisons between

![Figure 3. Typical optical emission spectrum of Ar/air plasma.](image)

![Figure 4. Typical optical emission spectrum of Ar/air plasma between 700 and 900 nm.](image)

![Figure 5. Typical optical emission spectrum of the N$_2$ second positive system for $\Delta \nu = -2$ of Ar/air plasma.](image)
theoretically calculated and experimentally measured spectra of the second positive system (C^3Π_u and B^3Π_g) for ν = 0 and 1. In this study, we measured the band spectra under steady state conditions at the center of the reactor, where rotational and translational relaxation may be accomplished [24]. Therefore, it is considered that the rotational temperature is almost equilibrated with the gas temperature [25]. Figure 7 shows the rotational and vibrational temperatures obtained from the second positive system. The rotational and vibrational temperature range from 1200 K to 1450 K and from 4600 K to 6900 K, respectively. The rotational temperature increases slightly with increasing RF power, while the vibrational temperature increases linearly up to 600 W and then remains almost constant. The rotational temperature is higher than the vibrational temperature. It is found that an increase in RF power generally causes an increase in rotational temperature. This is because the collision frequency between ions and neutral particles increases as the plasma density increases, and a larger amount of kinetic energy is transferred to neutral particles. Since the gas temperature is assumed to be close to the rotational temperature, the measured rotational temperatures are considered to be quite reasonable. Therefore, the gas temperature is found to be 1200 K to 1450 K. The results indicate that plasma sustained by an inductively coupled plasma source has sufficient enthalpy for...
efficient vaporization of mists, including precursors, during plasma-assisted mist CVD.

5. Summary
Inductively coupled RF plasmas for plasma-assisted mist CVD have been characterized. It was found that the plasma density measured with a cylindrical Langmuir probe was as high as $1.2 \times 10^{11}$ cm$^{-3}$ and the electron temperature was 1.0 - 2.5 eV for Ar plasma. The gas temperature in the inductively coupled plasma determined from optical emission spectroscopy of N$_2$ molecular spectra was 1200 - 1450 K for an Ar/air plasma. These results indicate that a plasma sustained by an inductively coupled source has a high density for dissociation of precursors and generation of oxygen radicals during ZnO film deposition, and has sufficient enthalpy for efficient vaporization of mists during plasma-assisted mist CVD.

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