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Comparative and integrative study of Langmuir probe and optical emission spectroscopy in a variable magnetic field electron cyclotron resonance chemical vapor deposition process used for depositing hydrogenated amorphous silicon thin films

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ABSTRACT

An electron cyclotron resonance chemical vapor deposition (ECR-CVD) system applied in a hydrogenated amorphous silicon (a-Si:H) thin-film deposition process was diagnosed in-situ by using optical emission spectroscopy (OES) and a Langmuir probe. The optical actinometry technique was used to obtain the ratio of species concentration to the concentration of a trace gas (Ar). The electron temperature (T_e^{oes}) was estimated according to the spectrum intensity ratio of H_β to Hα or that of Si* to SiH*, and the two estimation approaches were evaluated by comparing the results (T_e^{LP}) of Langmuir probe measurement. The probe surface contaminants (a-Si:H) produced during in-situ measurement created errors in the measurement of parameters such as the electron temperature and density (N_e). The results indicated that, when a-Si:H was coated on the probe at thicknesses less than 150 nm, the errors were negligible. OES and Langmuir probe measurement were integrated and used to determine the dependence of the processing pressure and resonance magnetic field configuration on the properties of an a-Si:H film grown using ECR-CVD. When the process pressure was increased, the N_e, T_e^{oes} and T_e^{LP} decreased; moreover, the Fourier-transform infrared spectroscopy results indicated that structure factor (R^*) increased, and both the photosensitivity and hydrogen content (C_H) decreased. An analysis conducted using OES and Langmuir probe measurement revealed, that the decreased concentration of the H radical reduced the passivation effect, and surface diffusion decreased. Furthermore, the gas partial pressure exerted a substantial influence on OES measurement. The volatility of the Ar spectrum intensity equaled the product of the volatility of N_e and T_e^{LP} when the partial pressure effect is eliminated. Regarding the resonance magnetic field, the effects of plasma resonance position on film characteristics were substantial. The N_e decreased greatly when the distance between quartz and the resonance zone was increased.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) thin films featuring low defect densities and high photosensitivity have been developed [1,2], and these thin films have attracted a substantial amount of attention worldwide because of their potential application in the photovoltaic industry. The a-Si:H thin film solar cell did not meet expectations because of its low transfer efficiency, and light-induced degradation, and because it did not exhibit a salient reduction in cost [3,4]. However, more applications for a-Si:H thin-films have recently been developed [5–7]. Because the high quality and low defect density of a-Si:H thin films have repeatedly been emphasized and confirmed [8,9], optimizing the a-Si:H thin film deposition process has regained the attention of researchers.

In the past 30 years, numerous vapor deposition techniques have been developed and applied in a-Si:H thin-film process, such as radio frequency (RF) plasma enhanced chemical vapor deposition (CVD) [10], very high frequency plasma enhanced CVD [11,12], hotwire-CVD [13], photo-CVD [14] and electron cyclotron resonance (ECR) CVD. The main advantages of ECR-CVD are: (1) no electrode contamination; (2) ion-bombardment effects are slight; (3) high-density plasma can be generated at a working pressure below 10^{-2} Pa; and (4) the rates at which thin films are deposited are high [15–17]; moreover,

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ECR-CVD exhibits high potential for application in preparing high-quality a-Si:H films that feature few surface defects and low photocarrier loss. The vapor chemical reaction that occurs in the a-Si:H ECR-CVD process has not been delineated. The plasma characteristics included physical properties such as electron temperature (*Te*), electron density (*Ne*), and sheath potential as well as the plasma chemical composition, and both types of characteristic influence the chemical reaction that occurs during plasma-enhanced thin-film deposition.

Most previous reports that have discussed a-Si:H thin films grown using the plasma-enhanced CVD process have focused on the relationship between process parameters and the characteristics of the thin film, and have generally ignored the role of plasma characteristics in the CVD process [18–22]. Moreover, few studies on ECR-CVD have considered the correlations among the operating parameters, plasma characteristics, and thin-film characteristics comprehensively. Furthermore, one plasma diagnostic method, involves using the Langmuir probe to measure T_e, N_e, sheath potential, and other physical properties of plasma directly, and the probe is typically used in conjunction with inert gas rather than real process gas to prevent the surface of the probe from becoming contaminated [23–26]. It also represents the distortions in the Langmuir probe measurement that may be caused. Optical emission spectroscopy (OES) is a non-intrusive and real-time plasma diagnosis technique used to determine the composition of partial radicals in plasma. After the excited species return to the ground state or a lower energy state, the characteristic energy is converted into photons that are and emitted into the surrounding environment. Plasma phenomenon can be interpreted based on trends and variations in emission spectra recorded using OES. In addition, the ratio of the emission sensitivity of one excitation energy species to the emission sensitivity of another excitation energy species, such as emission sensitivity ratio of H_β to H_α and that of Si to SiH, has been used as an index of variation in T_e [27,28]; however, no direct evidence has been provided to confirm these theoretical methods. Thus, this study involved integrating OES and Langmuir probe measurement to diagnose ECR-CVD plasma characteristics, which were influenced by the process pressure and resonance zone. In addition, the correlations among the operating parameters, plasma characteristics, and thin-film characteristics were investigated. Furthermore, the effect of tip surface contamination on Langmuir probe measurement, and the OES analysis methods are discussed.

2. Experimental details

2.1. Apparatus and conditions for film formation

Fig. 1(a) shows a schematic representation of the experimental setup. The frequency of the microwave supply was 2.45 GHz ± 5%, and the power could be varied up to 1600 W. TE_{01} mode microwaves radiated into a cylindrical waveguide and transformed into microwaves of the circular polarized TE_{11} mode. The impedance matching between the microwave system and the plasma was adjusted by using a three-stub tuner to ensure that the reflected microwave power was as low as possible. The circular TE_{11} mode microwaves were passed through a quartz glass plate 90 mm in diameter and 30 mm in thickness, and were radiated into the resonance chamber with an inner diameter of 225 mm and a length of 200 mm. The distance from the quartz window to the substrate surface was 425 mm. To improve the film uniformity, the a-Si:H thin films were deposited using various magnetic field configurations. An adjustable dc circuit was used to power the magnetic coil system, thus enabling the position of the ECR plasma to be controlled. Fig. 1(b) shows the magnetic field distribution in the resonance chamber and the relationship between the main coil current and the ECR plasma position. Argon, silane (SiH_4), and hydrogen, which were used as working gases, were injected into the resonance chamber from an upstream location (H_2) and to a downstream location (SiH_4, Ar), and the relative location between the ECR plasma and the process gas was regulated by modifying the main coil current. The a-Si:H films were deposited onto Corning Eagle XG glass substrates, and the deposition conditions are shown in Table 1.

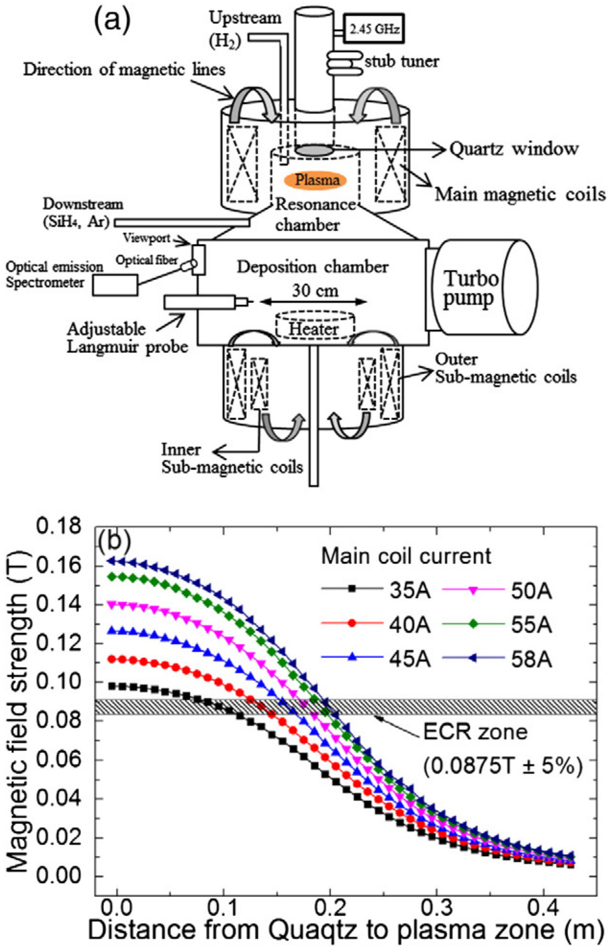

Fig. 1. (a) Schematic diagram of the experimental apparatus. (b) Dependence of the magnetic field distribution in the resonance chamber of main coil current.

2.2. Plasma characterization

2.2.1. Langmuir probe

A homemade Langmuir probe was used to measure the plasma potential, N_e, and ion density inside the deposition chamber during the ECR-CVD process. The probe was inserted into the chamber 2 cm above the substrate. The Keithley 2400 Source Meter supplied probe voltage ranging between −50 V and 50 V, thus enabling the current–voltage (*I–V*) curve to be obtained. When the electrons in the plasma

Table 1
ECR-CVD process parameters for different sets of a-Si:H films.

Process parameters	Setup values
Microwave power density (w/cm^2)	2
Substrate temperature (°C)	180
Background pressure (Pa)	4×10^{-4}
Working pressure (Pa)	0.4/0.667/1.333/2
Main(resonance) coil current (A)	35/45/58
Ar flow rate (sccm)	40
H_2 flow rate (sccm)	15
SiH_4 flow rate (sccm)	45