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Experimental Investigation of ZnO Thin Film Formed by Use of Negative Oxygen Ion Plasma and DEZn I

酸素負イオンプラズマとDEZnを用いたZnO薄膜生成実験 I

- 低温プロセスに対する酸素負イオンの効果 -

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In order to investigate a new plasma process at lower temperature, the use of negative ions is studied. Lots of negative oxygen ions are generated by a pulsed 13.56 MHz inductively coupled plasma discharge. The ion density measured by a probe-assisted laser photo-detachment method is about 10^{10} cm^{-3}. Preliminary data show that FWHM of XRD patterns change slightly with changing the bias voltage applied to the substrate holder.

1. Introduction

From a mass production point of view, industrial plasma sources capable of generating high density and uniform plasmas have been intensively studied for past several decades [1-5]. However, if we consider a next ultra-fine nanoscale process, the plasma source must be the one which alleviates damages due to plasma particle flux and the UV light emitted from plasma sources [6].

Considering oxygen O plasma processes, positive oxygen ions O^+ are usually produced. The ionization energy of O^+ is 12.7 eV so that the plasma temperature is not lowered [7]. However, if the primary role of O^+ was to transfer its kinetic energy to other particles and the substrate, O^+ would not be always needed. Alternatively, negative oxygen ions O^- may be used. Generally, O^- can be produced by the dissociative electron attachment process. In this case, the required energy is 4.7 eV [8], which is much lower than the O^+ case. In fact, there is a report showing that the oxidation of silicon has proceeded at low temperature by using O^- [9,10].

To investigate a possibility of developing a lower temperature process by use of O^-, we have just initiated a new experiment [11-13] on the ZnO process. It is a kind of plasma enhanced metal organic chemical vapor deposition (PE-MOCVD) [14-17]. In this conference, we present objectives, the detail of the prototype apparatus, and several initial data on the produced ZnO films.

2. Apparatus

2.1 *DEZn as Zn source*

Regarding a zinc source, we have employed diethyl zinc (DEZn), because it can be easily vaporized in vacuum. This property allows DEZn to transport into a reactor chamber without degrading the vacuum degree. At the first experiment, DEZn has conveyed without any help of carrier gas. But, at the next experiment, we will control the flow rate of DEZn (< 10 sccm) by using a mass flow controller (SEC-8440F, HORIBA Ltd.). Also, a carrier gas will be used with it. Because, the amount of DEZn seems to be much, according to the first experimental data.

2.2 *Reactor chamber*

The reactor chamber is a 20 cm diameter and 22 cm long cylindrical stainless steel (SUS304) which is a non-magnetic material. Above the reactor chamber, a 4 cm diameter 20 cm long Pyrex tube is set. Around this tube, a small helical antenna made of a copper sheet is wound. Both the length and width of the antenna are 5 and 1 cm, respectively. To this antenna, a 13.56 MHz RF power is fed through an impedance matching circuit that can control the duty cycle of the RF launching.

2.3 *Production of O^-*

To generate O^-, we have employed a pulsed discharge. Since the RF power is intermittently turned on/off [17], the electron temperature can be lowered enough to produce O^- through the process of the dissociative electron attachment [8]. Another reason for using the inductive discharge is that the contamination problem due to metal electrodes can be avoided. As for oxygen gas, it is introduced continuously by a mass flow controller (FCST1005L, Fujikin Inc.). The value of gas pressure is variable but fixed to be at ~ 10 Pa in presented experiments. To monitor the value exactly,

a ceramic capacitance manometer (CCMT-1D-034, ULVAC Inc.) will be installed.

2.4 *Diagnostics*

Regarding diagnostics, the O^- density is measured by a laser photo detachment method [18] with a laser diode (L8828-62, Hamamatsu Photonics Inc.). The laser outputs 1 W at λ = 808 nm. To measure the photo detachment electrons, we have so far used a square tip in shape with 0.5 x 1 cm in height and width and 0.01 cm in thickness. Typical values of O^- density measured by this probe is about 10^{10} cm^{-3} [11]. In experiments, a video camera has been sometimes used to record the plasma discharge. Also, we have been developing several probes to measure distributions of plasma space potential and O^- plasmas.

3. Preliminary Results

We have been performing the first series of experiments. Readers can also find information about the research in two companion papers [12,13]. The main purpose is to investigate whether any effect of O^- on the process appears or not. One example will be presented below.

Figure 1 shows dependences of the FWHM of XRD patterns on the bias voltage V_b applied to the substrate holder. As seen from the plotted data, except for the case of V_b = 80 V, values of FWHM become smaller with increasing V_b. Since the smaller FWHM reflects a bigger grain size of ZnO particles, the data suggest that O^- is possibly accelerated towards the substrate surface.

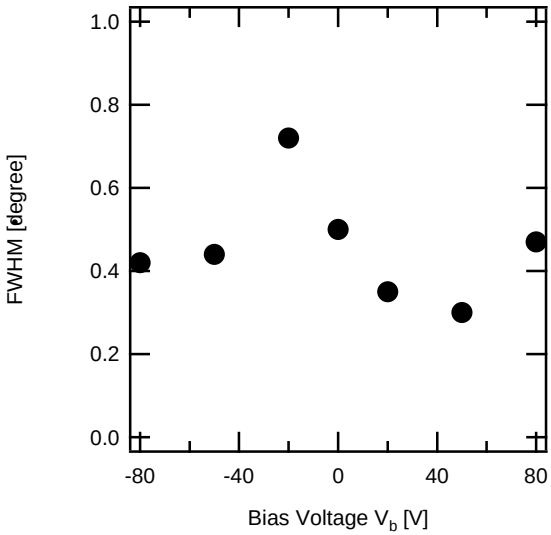

Fig. 1 Dependences of the FWHM of XRD patterns of the formed ZnO film on V_b.

And then, O^- may transfer its kinetic energy to the substrate, which could enhance surface mobility. Anyhow, further measurements are required. The detail will be presented in anywhere.

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