Plasma synthesis of ZnO transparent conductive film for multi-junction solar cells

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1. Introduction

Transparent Conductive Film (TCF) is a fundamental material for electronics equipments such as flat display panel, solar cell, and transparent oxide semiconductor so on. ITO (Indium Thin Oxide) is well known as most popular TCF materials to fabricate their devices. However, the deeply doped material such as AZO, SnO_2:F as well as ITO is essentially never to be applied to the device with near-infrared sensitivity. Also Indium is rare material regardless of having the versatile functions. Undoped ZnO TCF whose property is small optical absorption coefficient over the near-infrared region, has been focused as the full spectrum TCF for the multi-junction solar cells and as the substitute material for ITO. Although several advanced processing methods such as CVD, PLD, and sputtering have been executed, the conductivity of ZnO is still poor than ITO so far. In order to improve properties of ZnO TCF, we employ the ion plating system based on introducing Zn vapor to Inductively Coupled Plasma (ICP) in the relatively low pressure oxygen gas. For the deposition on the dielectric materials, ICP can suppress the damage by ions incident upon the sample. As a result, it is expected to expand the transparent wavelength to the near-infrared region by the high mobility accompanying with higher crystallinity with less grain boundary. In Fig.1, one of our data is about to enter to the commercial region (dashed ellipse).

2. Experimental setup

After the zinc wire is set to the oven, the chamber is pumped to the pressure of 10^{-4} Pa order. For the oxygen flow rate of 10 ~ 40 sccm, the pure oxygen plasma around 0.1 Pa order is generated inside the quartz

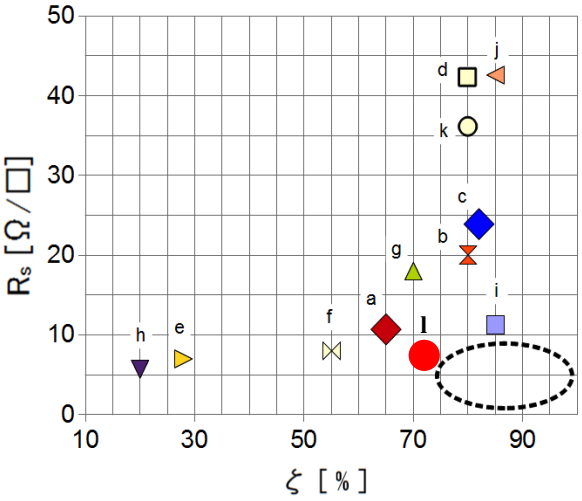

Fig.1 Mapping of the sheet resistance and the light transmittance for 1700 nm synthesized from a ZnO, b ZnO[(1)], c ZnO:H, d ZnO:H[(2)], e ZnO:Al, f ZnO:Al, g ITO, h ITO-AgCu-ITO[(3)], i In_2O_3:H, j In_2O_3:H k In_2O_3:Mo, and l ZnO. Data a, c and **l** are our results.

tube surrounded by the coil at which rf power feeds as shown in Fig.2. Zn vapor is introduced to the oxygen plasma by heating the Zn oven up to 500 °C. When the vapor is enough to change the color of excited gas from yellow to pink, the deposition is started at the opening of the shutter. The substrate is the unheated Pyrex glass, the surface of which is installed normally on the axis of the coil. The plasma parameter such as the plasma potential ϕ is measured with the Langmuir probe.

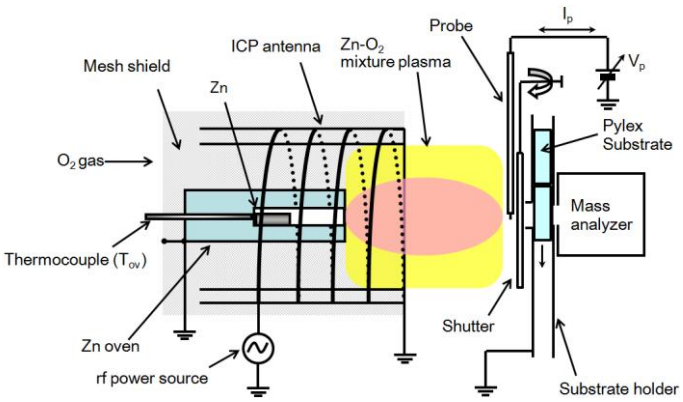

Fig.2 The schematic drawing of the experimental setup.

3. Experimental results and discussion

The plasma density n_0 increases with an increase of the net rf power ΔP. The plasma potential ϕ begins to decrease from ΔP =45 W, however, the electron temperature T_e keeps almost constant with an increase of ΔP in Fig.3. It seems that ΔP is almost consumed to ionize the oxygen gas and the plasma impedance becomes low and then the voltage drop $V_{rf}(t)$ between the coil edges is low, thereby ϕ is low. In Fig.4, the increment of n_0 yields the higher deposition rate, showing that the sheet resistance R_s decreases. The gradual decrease of the resistivity ρ could be contributed to the increase of the glass temperature. Here, it is very important of $<\zeta>_{2100}$ for ZnO TCF to keep almost constant in the region of these thicknesses < 500 nm. Also it is pointed out that the increase of n_0 prompts O_2 to dissociate.

In order to decrease R_s further, the film thickness d is increased after optimizing the conditions of the zinc-oxygen mixture plasma, as shown in Fig.5. As d proportional to the deposition time increases, $<\zeta>_{2100}$ gradually decreases and R_s rapidly decreases. However, ρ shows the minimum value around d = 800 nm. This is considered to minimize the resistivity at the optimum substrate temperature since the glass temperature increases by the ion bombardment with an increase of the deposition time.

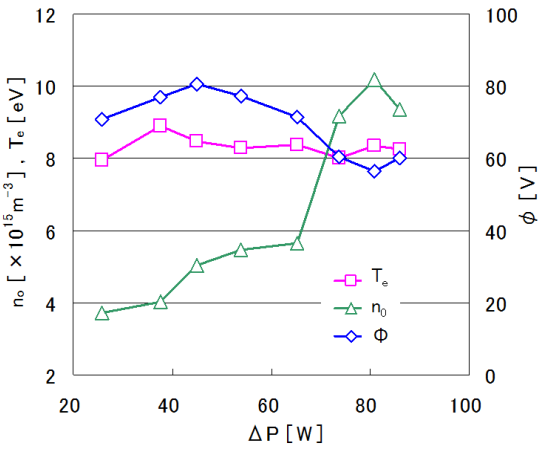

Fig.3 A ΔP dependence of plasma parameters.

By changing the ratio of Zn on O through regulating the oxygen flow rate, plasma density, and Zn oven temperature, the high performance properties with the sheet resistance of ~10 Ω/□ and the average light transmittance < ζ > over visible and near-infrared regions of 78 % is obtained on the unheated Pyrex glass as shown in Fig.6. < ζ > of undoped ZnO TCF (R_s =10.7 Ω) is better than that of the commercial ITO TCF (R_s =11.5 Ω) under the almost same sheet resistance. A main reason is seemed to be an incident of many oxygen atoms to the growth surface in ICP so as to suppress the occurrence of oxide defect due to the volatilization of oxygen molecular, satisfying the rate-limiting under the enough Zn vapor. This will lead the mobility to elevate sustaining the carrier density near and less than the critical carrier density which makes the plasmon effect to reflect the near-infrared light. Also adequate bombardment of ion accelerated in time-averaged sheath potential may push out the oxygen molecular at grain boundary and thereby the mobility may become high.

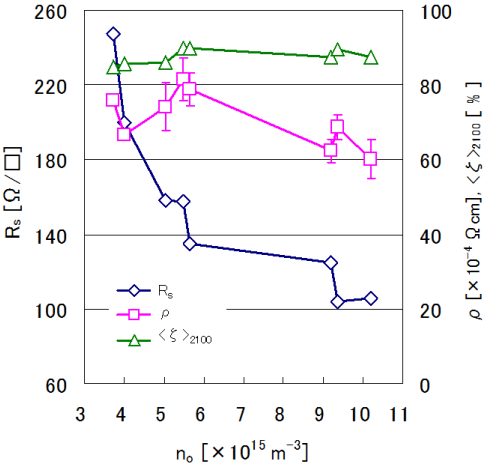

Fig.4 A plasma density dependence of ZnO properties. $<\zeta>_{2100}$ denotes the average light transmittance between 380 and 2100 nm wavelength.

Here let us describe that ICP excited by VHF in low pressure can provide the optimum energy of ions incident upon the insulated substrate for high quality ZnO TCF. Although V_{rf} (t) changes the radial plasma potential ϕ (t, r) through the quartz and the radial sheath, the dynamic range of ϕ (t, r) for ICP of the one turn coil is the same as that of the conventional CCP since the coil is insulated from the plasma through the quartz tube and thereby the radial rf self-bias occurs. At the same time, the electrons having the Fermi acceleration under ϕ (t, r) gain the large motion energy from the time-varying radial electric-field of the sheath at the inside wall of the quartz tube. Since the radial electron temperature $T_{e\text{-}r}$ increases due to the Fermi acceleration, the time-averaged plasma potential $<\phi(t, r=0)>$ on the axis of the coil increases with respect to the potential V_{DCr} at the inside surface of the quartz tube so as to

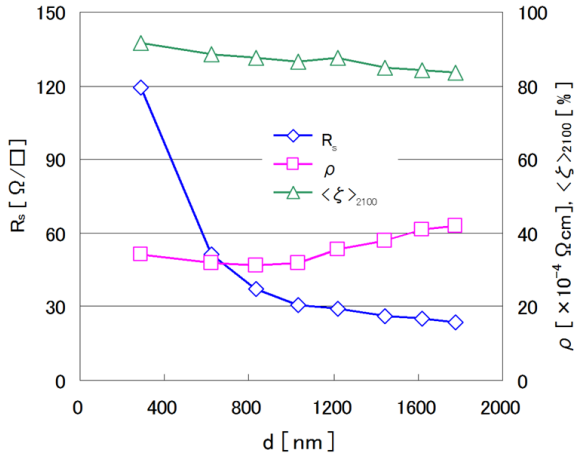

Fig.5 A ZnO film thickness dependence of ZnO properties.

satisfy the floating condition. V_{DCr} increases negatively with an increase of the plasma density n_0 due to the charge-up of plasma electrons. This supports a ΔP dependency of ϕ and n_0 in Fig.3. Next, why do we employ the VHF excitation ? In order to suppress the plasma loss due to the increment of $<\phi(t, r=0)>$, at the view point of electron inertia, this would be better to low $T_{e\text{-}r}$ than 13.56 MHz excitation. Finally, low pressure operation gives us the benefit as follows. Since the rf electric-field between the powered coil edge and the grounded substrate holder is smaller than one between the powered coil edge and the grounded oven and thereby the axial Fermi acceleration of electrons is small, $T_{e\text{-}z}$ also will be smaller than $T_{e\text{-}r}$ under low pressure of ~ 0.1 Pa although there is a thermal relaxation due to the collision of the radial trapped electrons. Therefore, in front of the growth surface on the Pyrex glass, the sheath voltage drop proportional to $T_{e\text{-}z}$ [4] is small and the maximum energy of ions accelerated in the collision-less sheath is W_i = 8 ~ 20 eV under the assumption that $T_{e\text{-}z}$ = $T_{e\text{-}r}$ / (2 ~ 5) considering the coil turn number and substituting T_e in Fig.3 to $T_{e\text{-}r}$. Values of these W_i range are considered to be reasonable for providing the high quality ZnO TCF since W_i is beyond the ZnO aggregation energy (1.89 eV) and is too small not to destroy the nucleation of ZnO crystal.

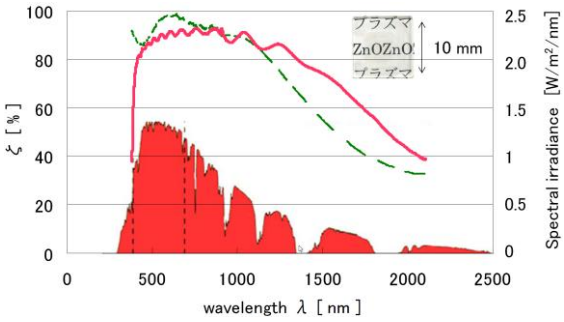

Fig.6 Dependences of optical transmittance on wave-length for ZnO (——) and ITO (- - - -) films. An insert photo is ZnO film synthesized on the Pyrex glass. A wave-length dependence of solar spectral irradiance also is showed as solid-filled area.

4. Summary

We have synthesized the high quality ZnO TCF expandable to the near-infrared region with keeping the sheet resistance less than 10 Ω/□. Top data (label **l** in Fig.1) is 7.4 Ω/□ with the light transmittance of 71 % at 1700 nm. Although the thickness increases up to 2900 nm, our ZnO TCF is expected to apply as the transparent electrode of the multi-junction solar cell. To explore more optimum processing condition, a time-spatial measurement of the plasma property with focusing on less $T_{e\text{-}z}$ is indispensable.

References

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