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# Development of Multi-junction technique for Semiconductor substrates by using Transparent and conductive polymer for Solar cells' application

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**Abstract.** The mechanical stacking technique was developed for multi-junctions of semiconductors by using transparent and conductive polymer (poly-thiophene: PT). In order to promote the multi-absorptions within stacked solar cells, ZnO powder was selected for the light scattering agent adding to PT. ZnO powders were synthesized by vacuum evaporation from Zn in oxygen partial pressure of 100 Torr, and *ex-situ* oxidization was carried out at 900°C in the air. Aggregated ZnO powders were characterized by Raman scattering, FT-IR and impedance analyzer. The molecular orbit (MO) calculation was carried out for PT. The energy gap between highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) was estimated by extended Hükel MO method. A PT film was spin coated on Si substrates of their binder, and then the substrates were connected. The *I-V* properties of PT films were measured with *p*-type and *n*-type Si substrates.

## 1.Introduction

The energy consumption has been increased from 1970's, and that should be prevented and modified by ecological technologies with producing new energy. Therefore several energy generation devices (solar cells, thermoelectric power) and apparatus (wind power, geothermal power, hydroelectric power generations) have been produced to be generating and recycling new energies.[1] Si solar cell was innovated by M.D. Chapin and M. B. Prince et al. [2], and several materials have been investigated about their potentials for solar cells' applications. The crystal and amorphous Si as tandem type cells have been developed with increasing of demands in commercial product use. Recently, stacked type solar cells such as Si and $SiO_2$ (quantum dot) multi-layer have been proposed in order to attain highly quantum efficiency.[3] The merit of stacked type solar cells is possible to control the energy band and mini-gap suited for the sunlight spectrum. Sunlight shows an air mass spectrum (AM1.5) on the ground. The AM1.5 spectrum can be separated to three region (ultraviolet, visible, infrared) spectra. These lights can be absorbed by wide, middle and narrow band-gap semiconductors.[4] **Figure 1** shows the AM1.5 and concept of multi-junction solar cells aiming highly sunlight absorption and electrical power generation. We have tried to fabricate multi-junctions of semiconductor substrates by using transparent and conducting polymer.

Transparent and conductive oxides (TCO) such as ZnO have been attracted for upper electrodes on the solar cells because of its transparency and conductivity. As shown in **Fig. 1 (b)**, we focus on ZnO powder as light scattering agent that is returning back a part of light to absorbers (semiconductors), and is adding to the junctions (polymer). In this paper, we present the ZnO powder preparation, polymer coating and connecting Si substrates, and their optical and electrical properties in order to fabricate multi-junction solar cells.

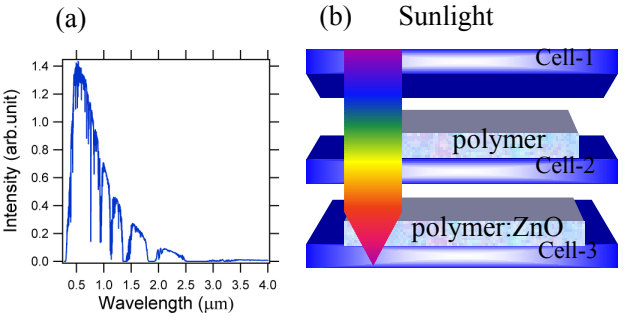


**Fig.1:** (a) Air-mass 1.5 spectrum (AM1.5). (b) The concept of multi-junction solar cells in this study. The cells can be selected wide (cell-1), middle (cell-2) and narrow (cell-3) band-gap semiconductors. The cells are connected by transparent and conductive polymer films with light scattering agent (ZnO powder).

## 2. Experimental

2-1 *Preparation of ZnO powder*

ZnO powders were synthesized by vacuum evaporation system equipped with a Knudsen cell (K-cell) in the partial $O_2$ pressure of 100 Torr. The Zn was selected as a source material. Zn was heated by a K-cell, and evaporated at melting point (420$^o$C). **Figure 2** (a) shows the preparation system and (b) photograph of synthesized ZnO and Zn powders. (c) Standard ZnO powder (NewMet-Koch., 6N, grain size: less than 127$\mu$m) was confirmed as (d) aggregate bodies by colloidal deposition of acetone dispersion media in order to measure the optical and electrical properties.

In order to promote oxygen vacancies and creation of carriers, the oxygen reduction process was carried out for ZnO aggregated bodies by carbon powder in $Al_2O_3$ crucible at 900$^o$C in the air (0.5-5h).

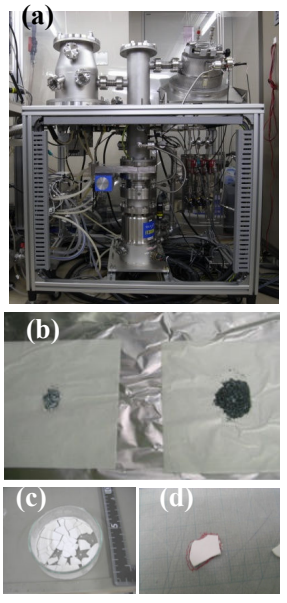


**Fig.2:** (a) Powder preparation system, (b) ZnO, Zn powders, (c, d) ZnO aggregated bodies prepared by colloidal deposition method.

2-2 *Polymer*

**Figure 3** shows (a) the molecule structure and (b) wave functions of PT. PT confirms the hetero-cyclic compound ($C_5H_5$) substituted with sulphur and cyclic hydrocarbons ($C_6H_6$). PEDOT (Aldrich) and Denatoron-G115s (Nagase) were selected in this study. PT films were coated on Si (10x20mm$^2$, 525$\mu$m) and Ge (10mmx10mm$^2$, 150$\mu$m) substrates by a spin coater (Active, ACT-300AII).

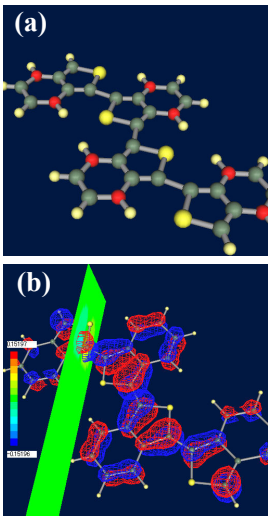


**Fig.3:** (a) Structure and (b) electronic structure of poly-thiophene (Yellow: S, Dark green: C, Red: O, Light yellow: H atoms).

2-3.*Molecular orbit calculations*

Following Hückel method, wave function ($\phi$) of $C_nH_n$ is written by $\phi_j=\Sigma c_{jm}\chi_m$ and $c_{jm}=(1/(n)^{0.5})\exp[i2(j-1)\pi m/n]$, where $m$, $j$=1, 2,.., $n$. The eigen-energy is also $\varepsilon_j=\alpha+\lambda\beta=\alpha+2\beta\cos[2(j-1)\pi/n]$, where $\alpha$, $\lambda$, and $\beta$ are Coulomb integral ($=\int \chi_i h \chi_i$), eigen-value and resonance integral ($=\int \chi_i h \chi_j$), respectively. A sulphur ion act as hetero-cyclic compound in $C_5H_5$ of PT, and $\beta$ is modified to be $\beta_S=0.5\beta$.[5] The molecular orbits (MOs) calculations were carried out for PTs by conventional extend Hückel MO method using software (WinMoStar), as shown in **Fig.3**.[6]

2-4. *Characterizations*

The crystal structure, lattice constants and crystallite sizes of ZnO powders were estimated from x-ray diffraction pattern (XRD, Rigaku RAD-IIc). Optical phonon vibrations of ZnO aggregated bodies (as powder state) were observed by $\mu$-Raman scattering (RENISHAW, $Ar^+$:514.5nm, 10mW, spot size:5$\mu$m). Fourier transformed infrared spectra (FT-IR, JASCO-6100) were also measured for ZnO aggregated bodies (transmittance, reflectance) and PT films (transmittance). Dc resistance ($R$) and frequency dependence of impedance ($Z$) of ZnO aggregated bodies (coated with Ag electrodes) were measured by using digital multi-meter (Agilent U1252A) and LCR meter (Hioki 3532: 40Hz-5MHz), respectively. Current versus applied voltage ($I$-$V$) characteristics of

stacked Si/PT/Si structure were measured by a precision semiconductor parameter analyzer (Agilent 4516c) at room temperature.

## 3. Results and Discussion

3-1 *Properties of ZnO aggregated bodies*

Crystal structure, lattice constants, crystallite size of ZnO powders were estimated to be Wurtzite ($C_{6v}$), $a$=0.3247nm, $c$=0.5.2022nm and 0.635nm from XRD patterns, respectively.

**Figure 4 (a)** shows the $\mu$-Raman scattering spectra of ZnO powders as (random polarization configuration) the functions of oxidation and reduction process (dots). Particularly, Raman peaks at 330cm$^{-1}$ of ZnO powder were slightly decreased with increasing reduction processing time, although density of ZnO aggregated bodies was kept around 3g/cm$^3$ as shown in **Fig.4 (b)**. The irreducible representation of ZnO is $\Gamma$=$A_1$+$B_1$+$E_1$+$E_2$. Hence, Raman peaks at 330cm$^{-1}$ and 436cm$^{-1}$ are $A_1$ and $E_1$. In order to estimate the relation between optical phonon vibration and oxygen vacancies, Raman spectra were curve fitted by Gauss functions (solid lines). **Figure 4 (c)** shows the results of curve fit about $A_1$, $E_1$ peaks and $A_1$/$E_1$ ratio. From $A_1$/$E_1$ ratio, $A_1$ peak ($c$-axis vibration: 1 direction) is sensitive for oxygen vacancies, but $E_1$ peak ($a$-$b$ axes vibrations: 2 directions) is insensitive because of possible vibration directions.

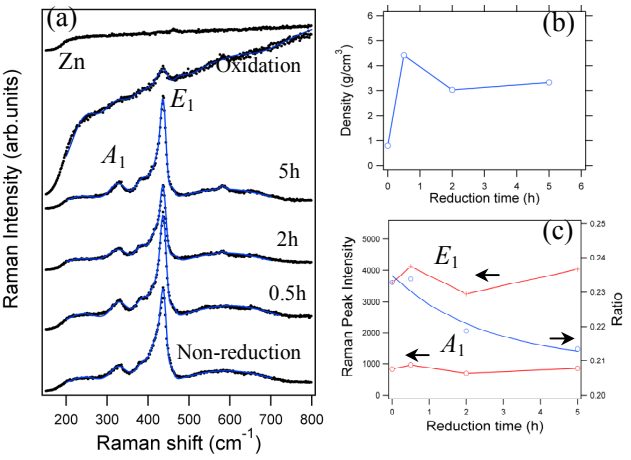


**Fig.4:** (a) $\mu$-Raman scattering spectra, (b) density and (c) $A_1$ and $E_1$ peak intensities and ratio of ZnO aggregated bodies as the functions of oxidation and reduction processing time.

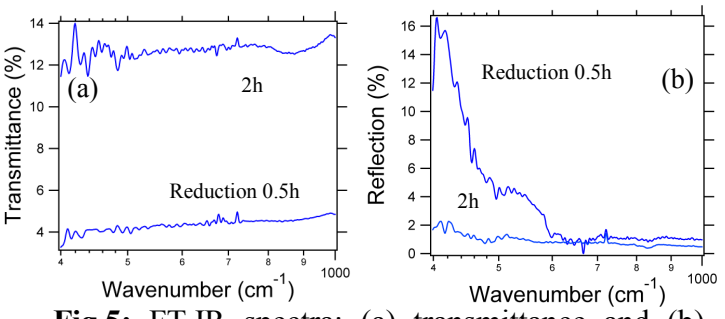


**Fig.5:** FT-IR spectra: (a) transmittance and (b) reflectance configurations of ZnO aggregated bodies.

**Figure 5** shows the FT-IR spectra of ZnO aggregated bodies. Transmittance showed less than 14% in the infrared region because highly random scattering effect was appeared on the surface. Transmittance was increased with increasing the reduction processing time. In addition, optical vibrations were weakly observed around 410cm$^{-1}$. Reflectance shows also optical phonon peak at 410cm$^{-1}$. The intensities of the peaks were on the other hand decreased with increased reduction processing time.

**Figure 6** shows the frequency dependence of Z of ZnO aggregated bodies. As a function of reduction time, ZnO was decreased Z. Lower than 3kHz, a few of shoulders are observed by polarization among grains of ZnO. Polarization among grains is cased by Schottky contacts. Grain contacts would be drastic

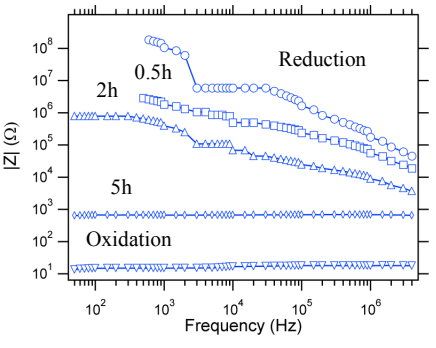


**Fig.6:** Frequency dependence of impedance for ZnO aggregated bodies as a function of oxidation and reduction processing time.

changed as a function of reduction processing time. [8] From dc measurements, *R* of ZnO aggregated bodies decreased from 100MΩ to 10Ω with increasing oxygen vacancies. Therefore, prepared ZnO powder is conductive and light scattering agent, and it could be adding into transparent and conductive polymer (ceramic composite).

3-2 *Molecular orbit levels' estimations about poly-thiophene*

The PT has been known as a transparent and conductive polymer. Highly conductive polymer: PEDOT-PSS, PEDOT and Denatron-G115s are attracted for transparent functional devices as the electrodes on organic and/or inorganic materials, and the applications of dye-sensitised solar cells and organic electro-luminescence (EL) devices have been reported.[9]

In order to estimate electrical contact between PT and Si, the MO calculation of PT (*n*EDOT) was tried by extend Hückel MO method. **Figure 7** shows MO levels of PT (4EDOT). The energy gap of 4EDOT (Quinoid type) between HOMO and LUMO was estimated to be 5.34eV (ascribes transparent; 4-4.8eV is reported from 14EDOT with 8 stacked layers: Diradical type), and gap between nearest MO level and Si (1.12eV) is estimated to be 0.08-0.18 eV (Ohmic contact). It would be a possibility for Ohmic contact between PT and Si.

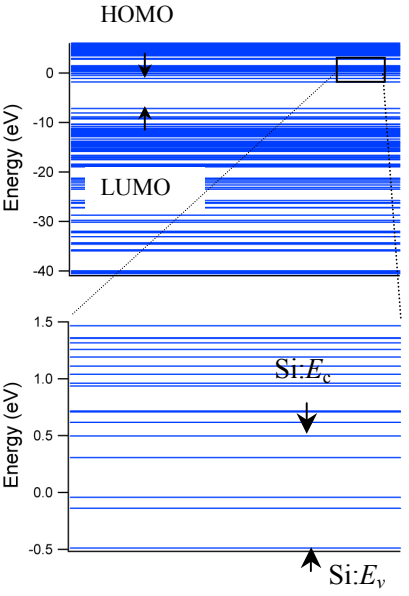


**Fig.7:** Estimated MO energy levels of poly-thiophene, and a possible Ohmic contacts for conduction and valence bands in Si.

3-3 *Transmittance of polymer composite and I-V characteristics of Si/PT/Si*

Finally, in order to estimate transparency and conductivity of PT (Denatron:G115s), we make a junction tentatively between glass and p and n-tyep Si substrates by using PEDOT and Denatron-G115s. **Figure 8** shows (a) transmittance spectrum of polymer composite (Denatron-G115s with ZnO powder 8-14vol%) on glass substrate and (b) *I-V* characteristics of Si substrates connected by Denatron-G115s. Fundamentally, PT is possible to be controlled as p-type (removing electron), as n-type (introducing electron), and is known as Bi-polaron conductor. Unfortunately, the polymer (Denatron-G115s) would be mainly act as p-type conductor, but we should focus on the linearity around lower voltage region. As a next step, we should be decreasing *R* in the junction due to modifying connect conditions (polymer state, surface process of Si substrate).

So as to use the multi-junction solar cells, polymer should be considered the aging effects under focussed sunlight irradiation and Joule-heating. Particularly, ultraviolet cuts the MO bonds in polymer, and thermal heating oxidizes polymer. As a merit in this study, however, we can use thick wide band gap semiconductor at top position (cell-1 in

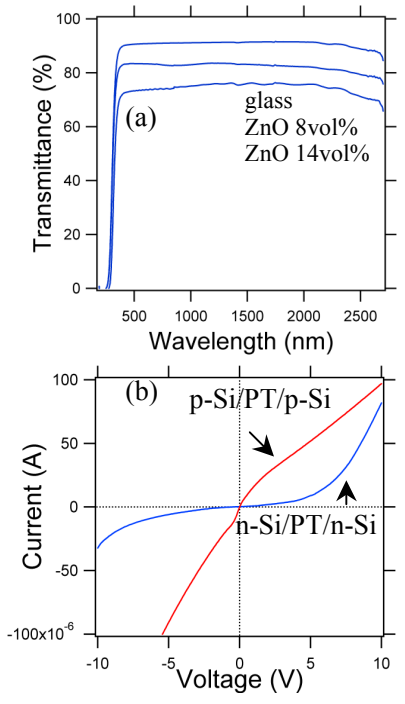


**Fig.8: (a)** Transmittance of polymer composite between glasses and **(b)** *I-V* characteristics of Si/PT/Si stacked structure.

**Fig.1**(b)) in order to absorb ultraviolet light. In addition, oxidization effect should be investigated in future study.

## 4. Conclusion

ZnO powders were synthesized, and were characterized by optical phonon's vibrations, light scattering and electrical properties as a function of oxidation and reduction processing time. From molecular orbit (MO) calculation for poly-thiophene (PT), energy gap between highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) of PT was estimated, and a possibility of Ohmic contact between PT and Si was obtained. Si substrates were tentatively joined by PT, its *I-V* property was measured with light illumination. Non-linearity in *I-V* property was considered not only conduction type but polymer state and surface process of Si substrates.

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