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Optical Characteristics of Conductive Polymer Polyaniline PANI-EB

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Abstract: *Semiconductors materials have the conducting properties in between conductors and insulators. They have wide range of applications in the field of electronics and optoelectronic devices. Silicon compounds are mainly used as semiconducting materials, but the method of production is very costly. Hence, the organic semiconductors materials can be considered, because of cheap raw materials for synthesis and their mode of construction or design. One of the organic semiconductors like Polyaniline (PANI) can be considered because of its aromatic ring and lone pair of electrons on nitrogen for conducting electricity. It is a cheaper cost, easily synthesizable and environmentally stable compound, with exciting electrochemical, optical and electrical properties. The synthesis was done by oxidation of aniline using hydrochloric acid HCl and ammonium persulphate (APS), which forms an emeraldine base EB. It was characterized by FESEM, XRD, FT-IR and UV-Vis Spectrophotometer.*

Keywords: *Organic Semiconductors, PANi, environmentally stable, XRD, FT-IR, and UV-Vis.*

I. INTRODUCTION

Semiconductor materials have attracted much interest during the past decade in both fundamental reaches and technical applications due to their optical and electrical properties [1]. Polymer based semiconductors are in the ocre of development because of their easy and cheap synthetic procedures. The optical, chemical and electrical properties have provided a tremendous scope in the field of electrical conductivity compared to metallic counter parts. Conductive polymers like polyaniline and polyacetylene have been subjected to numerous investigations in the past two decades [2, 3]. Polyaniline is an excellent example of a conjugated polymer. The nano fibers of polyaniline can be specifically synthesized for the application like rechargeable batteries [4], biosensors [5], corrosion protection layers [6], and separation membranes [7] and for molecular electronic materials. It is a cheap, easily synthesizable and environmentally stable compound, with exciting electrochemical, optical and electrical properties. Many of methods like chemical oxidative polymerization, hard templates [8, 9], seeding [10], and electrochemical synthesis [11] have been reported. We prepared the polyaniline by chemical oxidation polymerization of an aniline using hydrochloric acid and ammonium persulphate (APS), which forms an emeraldine salt then converted to insulator structure of polyaniline as emeraldine base which shows good microstructure, optical properties. These properties were characterized by FESEM, XRD, FT-IR and UV-Vis Spectrophotometer.

II. MATERIALS AND METHOD

The chemical agents required were procured from Merck chemicals. Aniline monomer was first distilled before the use. The catalyst, hydrochloric acid and oxidant agent ammonium persulphate APS were used as they were. The water used was double distilled. First aniline was distilled and stored in a clean bottle. 2ml of distilled aniline was dissolved in 1M 100ml hydrochloric acid. Exactly weighed 6gm of ammonium persulphate APS, the oxidant was dissolved in 100ml 1M hydrochloric acid. About 20ml of APS solution was added to the aniline solution drop wise with constant stirring and kept for overnight 24 h undisturbed. The obtained green polyaniline was washed with 1M hydrochloric acid to remove unreacted aniline, then with distilled water to remove APS tracks in the material, then treatment with acetone to remove any organic impurities. Then filtered material was dried at 80°C for 6 h and stored in tight container.

III. CHARACTERIZATION

The synthesized a conductive polymer was used to study the morphology of polymer structure through FE-SEM. The FE-SEM Morphological study of the thin films of PANi was carried out using by field effect scanning electron microscopy FE-SEM (Model: FEI Nova Nano SEM 450) operating at 20 kV. The Fourier Transfer Infrared spectrum was used for the analysis of functional groups of the polymer, with the help of Perkin Elmer (Model: Perkin Elmer Spectrum Gx) was studied in the frequency range of

400–4000 cm^{-1} . UV-Visible the spectrophotometer of the samples which were dispersed in demonized water under ultrasonic action, which were recorded on a used for the analysis band gap of energy using the instrument Shimadzu -1800 UV-vis spectrophotometer.

IV. RESULTS AND DISCUSSION

Field emission scanning microscopy FESEM images, as shown in the Figures 1 (a, b) demonstrate the morphology of polyaniline undoped emeraldine base type of powder polyaniline. The image scanning of FESEM samples is taken at profound amplifications at $5\mu\text{m}$ and $10\mu\text{m}$.

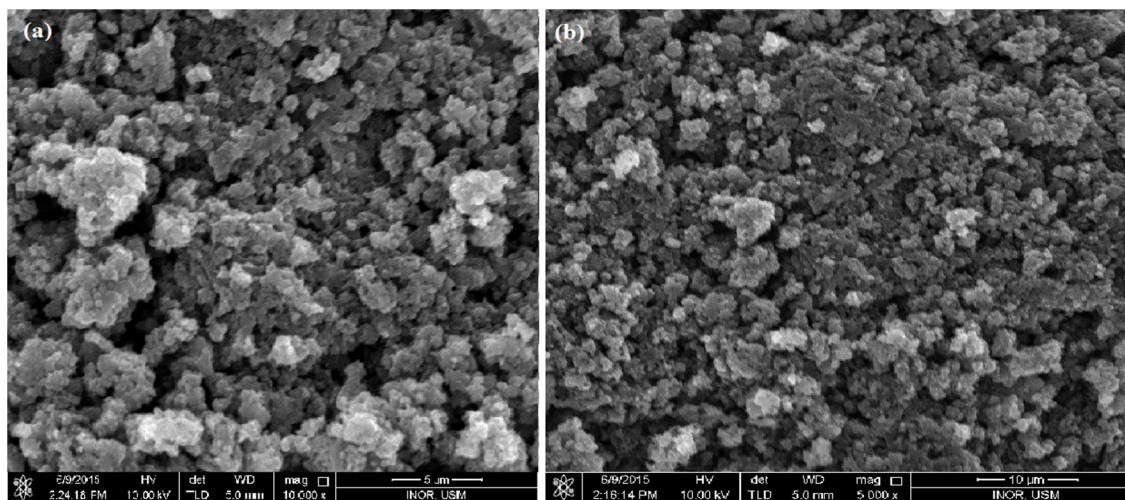


Figure 1: FESEM micrographs of polyaniline (EB) powder synthesized at (a) magnification to $5\mu\text{m}$ and (b) magnification to $10\mu\text{m}$.

The FESEM images show ordinary features of the polymer structure. All images are mostly made out of irregularly composed granular and flakes with sharp edges. In addition, the structure looks more porous. Figure. 1 demonstrate the morphology of polyaniline undoped (EB) powder prepared at 0°C . It can be seen that the polyaniline particles are highly micro-porous type morphology and able to increase the liquid–solid interfacial region [12- 14]. The exceedingly porosity nature of the polymer materials and the massed circular morphology was affirmed with a FESEM study.

XRD studies were done by using high resolution x-ray diffraction (PANAlaytical X-PERKY Pro MRD PW3040). XRD patterns were recorded in the range 2θ from 20° – 60° with step width 0.02° using $\text{CuK}\alpha 1$ radiation at $\lambda=1.5406\text{\AA}$. The observed diffraction peaks agreed well with the standard card of polymer with orthorhombic structure.

Figure 2 representing the x-ray diffraction of immaculate polyaniline (pure) PANI-EB demonstrates a peak at 22.73° ; this means the polyaniline is an amorphous nature material, these outcomes are in agreement with previous studies [15- 17].

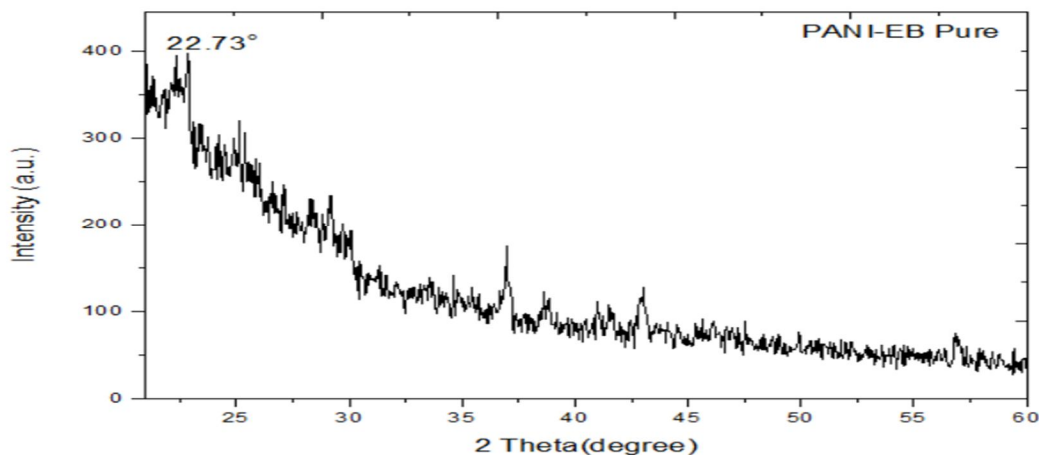


Figure 2: XRD pattern of Polyaniline pure.

For an orthorhombic structure can be estimated from the XRD information of all planes at 2θ values taking into account d -dispersing values. For the specimens, the constants have been resolved and are recorded in Table 1. The interplanar crystallinity distance d , and crystal size were calculated by Bragg's Law and Debye Scherer equation:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where k = Bragg's constant (0.9) and β is the full width half maximum (FWHM). The crystallite size D of the crystalline polymer is assessed with the full width half maximum FWHM intensity of the x-beam diffraction peaks at 2θ values utilizing Debye Scherrer formula.

Table 1: XRD-diffraction parameters of Polyaniline Samples.

| Polymer | 2θ (deg) | FWHM β ($^{\circ}$) | (hkl) | d (A°) | D (nm) |
|---------|--------------------|--------------------------------|-----------|-------------------------------|-------------|
| PANi-EB | 22.73 | 0.43 | (021) | 3.92 | 18.85 |

X-ray diffraction of pure polyaniline and doped powder prepared at 0°C showed the partial crystalline state increased as the molecular weight grew. The increase was more obvious for the samples prepared at low temperature. This may indicate that chains under lower temperature conditions have less structural defects.

Figure. 3 represents the FTIR spectra of pure polyaniline EB powder. The fundamental bands groups and their properties showed in polymer are determined. FTIR spectrum of polyaniline powder demonstrates the following four main vibrational bands groups: 1585 , 1301 , 1141 , and, 824 cm^{-1} . These are in incredible concurrence with already published materials [18-20].

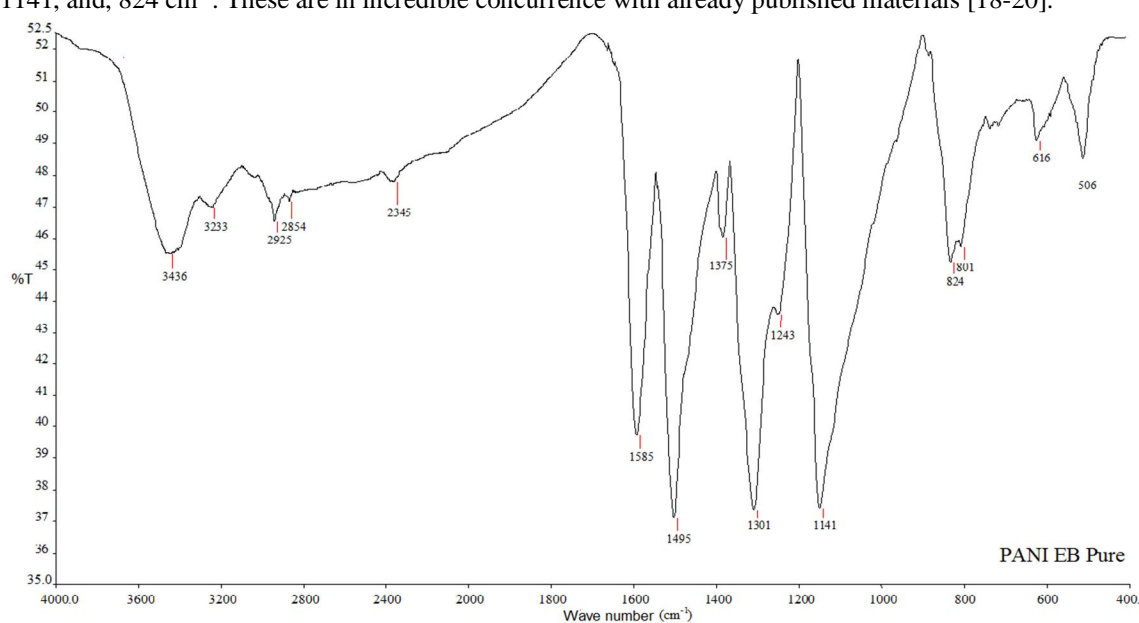


Figure 3: FTIR spectrum of undoped Polyaniline-EB powder.

The N-H stretching groups specified above represent for a non-bonded groups at 3436 cm^{-1} and N-H band at 3233 cm^{-1} . It is mostly important to note that the intensity of the hydrogen-bonded N-H stretching band is significant and higher than that of the free N-H band in PANI pure powder. This indicates synthesized EB is essentially self-associated with the hydrogen bonding.

These specific results are not perceived between chain hydrogen bonding of the different polyaniline molecules and intra-chain hydrogen bonding between different segments of the same polyaniline molecule. The groups near 824 cm^{-1} are property for the p-replaced chains and are found in all spectra with a little dislodging as shown by the preparation temperature. The band close to 1141 cm^{-1} is portrayed as being property for the conducting polymer because of the delocalization of electrical charges made by deprotonation and it can be attributed to groups' characteristics of B-NH-B or B-NH-Q where B assigns to the benzenoid sort rings

and Q to the quinoid sort rings [21]. In the locale around to 1300 cm^{-1} , the peak is attributed to the presence of aromatic amines in the polyaniline. The groups around $1500\text{-}1600\text{ cm}^{-1}$ are related to the stretching of the C=C and C=N bonds of the benzenoid and quinoid rings respectively. The bands of these groups give a thought of the oxidation condition of polymerization polyaniline; when they present comparable intensities, the polyaniline is in the emeraldine structure PANI-EB. There is evidence of a peak of low intensity in the area associated with O-H bond stretching around 3436 cm^{-1} due to the presence of moisture in the sample. All vibrational bonds of polymer are tabulated in Table 2.

Table 2: FTIR vibrational modes of PANI-EB.

| Wave number (cm^{-1}) | Assigned Functional Groups |
|----------------------------------|---|
| 3436 | O - H stretching bond |
| 3233 | N-H stretching |
| 3000 | C-H stretch |
| 1585 | C=N stretch in a quinoid ring |
| 1495 | C=C stretch in a benzenoid ring. |
| 1375-1141 | C-N bending |
| 800 | C-H (out of plane) of substituted aromatic ring |

UV- visible spectra were recorded from the synthesized Polyaniline using instrument Shimadzu 1800 UV-vis spectrophotometer. The Fig. 4 shows the UV-Visible pattern of Polyaniline. The spectrum has two peaks, one at 454 nm and other one at 800 nm. The first peak represents the presence of aniline moiety. The second peak represents the presence of benzenoid group and lone pair of electrons of nitrogen. This in turn leads to $\pi\text{-}\pi^*$ interactions of the molecule and this shows that it is a conducting polymer.

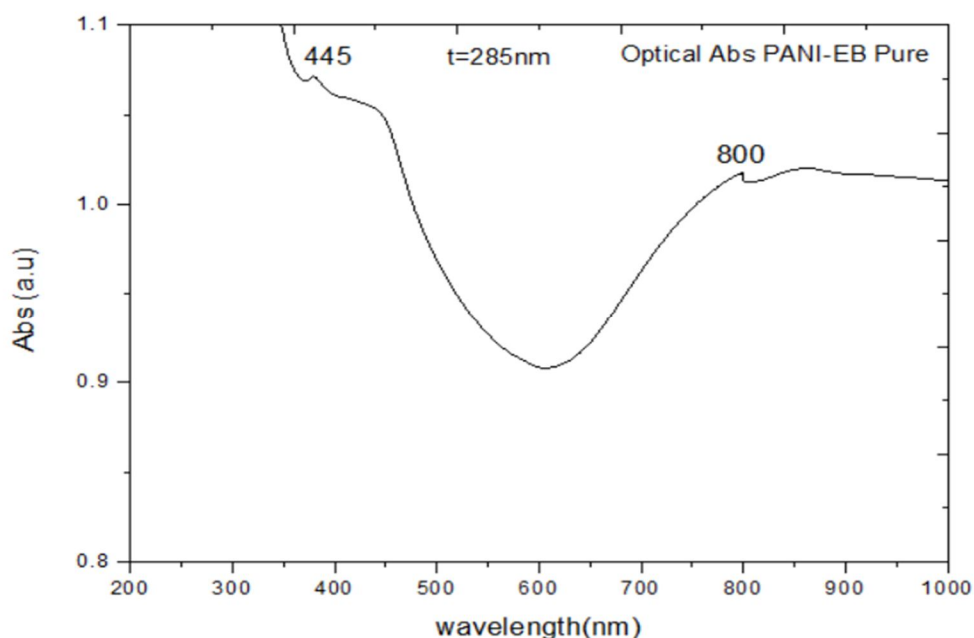


Figure 4: The absorption spectra of PANI-EB pure.

The highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital LUMO are separated by band gap which are fundamentally important, which it determines the electrical conductivity and optical absorbance of polyaniline. The band gap energy has been calculated by absorbance coefficient data as a function wave length using Tauc relation:

$$\alpha h\nu = B (h\nu - E_g)^n$$

where α is the absorbance coefficient $h\nu$ is the photon energy, B is the band gap tailing parameter, E_g is a characteristics energy which is termed as optical band gap and n is the transition probability index with discrete value like 1/2, 3/2, 2 or more depending on transition of direct or indirect or forbidden band gap. The absorption coefficient (α) at corresponding wavelength was calculated by using Lambert's relation.

$$\alpha = \frac{2.303 A}{l}$$

Where l is the path length and A is the absorbance. The plot $(\alpha h\nu)^{1/2}$ vs $h\nu$ was linear function existence of indirect allowed in transition in Polyaniline. Extrapolation of linear dependence of the relation to yield corresponding E_g .

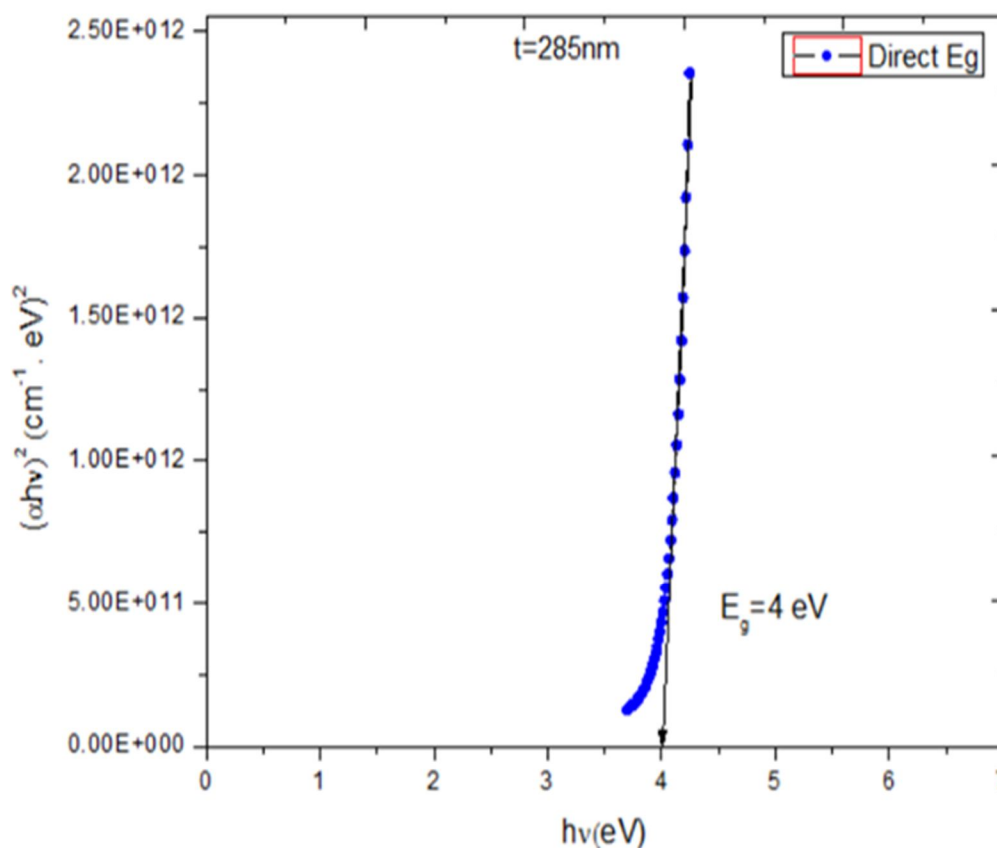


Figure 5: The energy gap for Polyaniline PANI pure.

The value of the optical energy of PANi synthesized obtained from Fig 5 is 4eV and this is due to $\pi-\pi^*$ transition from valance band to conduction band at 381 nm.

V. CONCLUSION

Polyaniline is show as one of the organic conductor. The optical properties show that it can even acts as an organic semiconductor. The morphology of polymer studied by XRD shows that, crystal size was 18.85nm, which is helpful for the $\pi-\pi^*$ transition, was studied through UV-Visible spectrophotometer. By this study, the band gap of the polymer was calculated through the Tauc's relation which was found to be 4eV. The properties of polyaniline show that, it is a p type semiconductor, which could be used in hybrid organic solar cell, where it may the conjugated with any inorganic n-type semiconductor such as TiO_2 or ZnO . By this one can expect a good output in the field of photovoltaic and optoelectronic device.

REFERENCES

- [1] Goswami M., Sahoo S., Meikap A.K., Gosh R., Characterization, optical and DC electrical properties of polyaniline and zinc sulphide nanocomposites, International Conference on Nanoscience Engineering and Technology, Chennai, 2011, 314-318.
- [2] Abdelaziz Rahy, Mohamed Sakrout, Sanjeev Manohar, Sung June Cho, John Ferraris, D. J. Yang, Polyaniline nanofiber synthesis by co-use of ammonium peroxydisulphate and sodium hypochlorite, Chemical Matter 20(15), 2008, 4808-4814.
- [3] Abdelaziz Rahy, Mohamed Sakrout, Sanjeev Manohar, Sung June Cho, John Ferraris, D. J. Yang, Polyaniline nanofiber synthesis by co-use of ammonium peroxydisulphate and sodium hypochlorite, Chemical Matter 20(15), 2008, 4808-4814.
- [4] MacDiarmid A.G., Yang L.S., Huang W.S., Humphrey B.D., Polyaniline: Electrochemistry and application to rechargeable batteries, Synthetic metals, 18, 1987, 393-398
- [5] Shabnam Virji, Jesse D. Fowler, Christina O. Baker, Jiaying Huang, Richard B. Kaner, Bruce H. Weiller Polyaniline nanofiber composites with metal salts: Chemical sensors for hydrogen sulfide, Small 1(6), 2005, 624-627
- [6] David W. DeBerry, Modification of the electrochemical and corrosion behavior of stainless steels with an electroactive coating, Journal of Electrochemical Society, 135(5), 1985, 1022-1026.
- [7] Charles R. Martin, Template Synthesis of Electronically Conductive Polymer Nanostructures, Accounts of chemical research, 28(2), 1995, 61-68
- [8] Hongjin Qiu, Meixiang Wan, Barry Matthews, Liming Dai, Conducting polyaniline nanotubes by template-free polymerization, Macromolecules 34(4), 2001, 675-677.
- [9] Xinyu Zhang , Warren J. Goux , and Sanjeev K. Manohar, Synthesis of polyaniline nanofibers by “nanofiber seeding”, Journal of American Chemical Society, 126(4), 2004, 4502-4503
- [10] K. Gopalakrishnan, M.Elango, M. Thamilselvan, Optical studies on nano-structured conducting Polyaniline prepared by chemical oxidation method, Archives of Physics Research, 3(4), 2012, 315-319.
- [11] C.H.Srinivas, D. Srinivasu, B. Kavitha, N. Narsimlu, K. Siva Kumar, Synthesis and characterization of nano size conducting polyaniline, IOSR Journal of Applied Physics 1(5), 2012, 12-15
- [12] Pawar, S. G. Patil, S. L. Chougule, M. A. Jundale, D. M. and Patil, V. B. (2010) Archives of Physics Research, 1(1), 57.
- [13] Gospodinova, N., and Terlemezyan, L. Prog, (1998) Polym. Sci. 2
- [14] Reka Devi, M. Lawrence, B. Prithivikumaran, N. Jeyaku, N. (2014) Internationa
- [15] Harada, I. Furukawa, Y. Ueda, F. (1989), Synthetic Metals, 29, E.30
- [16] Quillard, S. Louarn, G. Lafrant, S. MacDiarmid, A.G. (1994) Phys. Rev. B
- [17] Chen, L. Chen, W. Wang, J. and Chau-Nan Hong, F. (2004) Hydrogen-doped high conductivity ZnO films deposited by radio-frequency magnetron sputtering. Appl. Phys. Lett., 85, pp.5628-5630.



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