Bulk heterojunction blend (NiPcTs:PEDOT:PSS) in gas sensing

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Abstract

Thin films of bulk heterojunction blend Ni-Phthalocyanine Tetrasulfonic acid tetrasodium salt and dpoly (3, 4-ethylenedioxythiophene) poly (styrenesulfonate) (NiPcTs: PEDOT: PSS) with different (PEDOT:PSS) concentrations (0.5, 1, 2) are prepared using spin coating technique with thickness 100 nm on glass and Si substrate. The X-Ray diffraction pattern of NiPcTs powder was studied and compared with NiPc powder, the pattern showed that the structure is a polycrystalline with monoclinic phase. XRD analysis of as-deposited (NiPcTs/PEDOT:PSS) thin films blends in dicated that the film appeared at(100), (102) in concentrations (0.5, 1) and (100) in concentration (2). The grain size is increased with increasing (PEDOT:PSS) concentrations. FTIR measurements for these bulk heterojunction blend thin films also carried out in this work and gave good information about the bonds and their locations. Sensor measurements of Si/NiPcTS:PEDOT:PSS bulk heterojunctions blend thin films show a good sensitivity for NO_2 gas Compared to NH_3gas. The NiPcTS/PEDOT:PSS gas sensor device work at room temperature than high temperature for NO_2 gas but good sensitivity at100ºC for NH_3 gas and sensor work more effectively in 0.5 concentration for both gases.

Key words

Organic, semiconductor, phthalocyanines, gas sensor.

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المزيج الهجين من نيكل فثالوسايلين تتراسولفنك و بوليمر PEDOT:PSS كمتحسس غازي

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الخلاصة

حضرت أغشيه رقيقه من المزيج المتغاير نيكل فثايوسايلين تترا سولفينك والبوليمر الموصل PEDOT:PSS بتركيز (0.5,1,2) بطريقة الطلاء ألبرمي بسمك 100 نانومتر على الزجاج وشرائح السليكون. تم دراسة نمط حيود الأشعة السينية لمسحوق NiPcTs ومقارنتها مع مسحوق NiPc وقد تبين ان التركيب متعدد التبلور احادي الوجة. تحليل حيود الأشعة السينية للمزيج (NiPcTs:PEDOT:PSS) يبين، أن الاغشيه المحضرة عند التركيز (1, 0.5) تظهر قمم عند (102), (100) و (100) عند التركيز 2. الحجم الحبيبي يزداد مع زيادة تركيز(PEDOT:PSS). فحوصات FTIR أعطتنا معلومات جيده عن الأواصر ومواقعها. فحوصات التحسس الغازي للمزيج المتغاير المرسب على السيلكون (Si/NiPcTs:PEDOT:PSS) أظهرت تحسسية عالية لغاز اوكسيد النيتروجين مقارنة بغاز الامونيا .المتحسس الغازي لغاز اوكسيد النيتروجين يعمل بصوره افصل في درجة حرارة الغرفة مقارنة بالدرجات الحرارية الأعلى ولكن برجة 100ºC بالنسبة لغاز الامونيا ويعمل بصورة أكفأ عند التركيز 0.5 لكلا الغازين.

Introduction

These research areas are gaining attention due to the fact that the organic semiconductors enable precise organic synthesis, low-temperature fabrication processes on variety of both rigid and flexible substrates, and straightforward miniaturization of their devices [1]. The uses of organic semiconductors as sensors have

revolutionized modern technology in recent years due to their inherent capabilities. Organic Gas Sensors have been successfully developed in many applications to detect Humidity(both absolute and relative), various gases like Ammonia, alcohol, nitrogen oxides, chlorine, hydrogen etc. and nitro aromatic compounds based explosive vapors. A more appropriate selection of the optimal organic semiconductor is important by addressing the relationship of the surface chemistry of the sensor active material and its electrical response [2].

Highly pollutant and toxic gas like NO_2 in the environment has emerged as a major issue to public health [1] with the increase in automobile fuel vehicles and chemical industries. More disturbing fact is that NO_2 emanated from diesel once out in the air forms more harmful ozone gas.Several NO_2 solid gas sensors reported in the past. Phthalocyanines (Pcs) and structurally related compounds have been evolved as effective NO_2 gas sensors [3-5]. Phthalocyanine(Pc) is a conjugated heterocyclic 18-π electron containing compound. One of the important advantages of Pcs over other organic materials is their thermal and chemical stability. Metallophthallocyanines (MPcs) exhibit high sensitivity towardslower concentration of oxidizing and reducing gases such as NO_2, ozone, chlorine and bromine [6].

Ammonia gas sensors have emerged as one of the most demanding devices in the field environmental science and clinical diagnostics [6, 7]. Several efforts have been made to develop low-cost, highly sensitive and highly selective NH_3 gas sensors. Recent works have shown that device parameters like conductivity and the field-effect mobility of pentacene-based OFET significantly get affected by ammonia (NH_3) gas.

Experimental

The p-type organic semiconductors NiPcTs and PEDOT:PSS were obtained from Sigma-Aldrich without more purification. Fig.1shows the structure of the NiPcTs and PEDOT:PSS molecules .NiPcTs was dissolved in dyonoyiz water and mix well using magnetic stirrer to be homogeneous then prepared the three concentrations of PEDOT:PSS(0.5, 1 and 2). The glass was cleaned by water then acetone and alcohol, Si was etching by HF acid concentration of 0.1 for a ten minutes then was cleaning by acetone and alcohol. The thin films deposited using spin coater with 100nm thickness at room temperature, the spin rate was 1500rpm for time 1.5min on glass substrate and Si. All the samples prepared by using Laurell WS-650Mz-23NPP Spin coater.

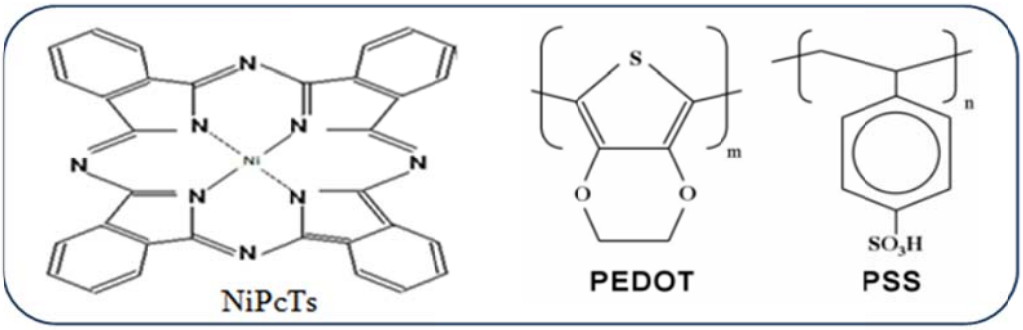

Fig. 1: Molecular structure of the NiPcTs and PEDOT:PSS molecules.

The X-ray diffraction and FTIR of film deposited on glass substrate and gas sensor deposited on Si substrate (Si/NiPcTS:PEDOT : PSS) are studied. The samples area is 0.5 cm^2 and treated at temperature T_a (100ºC) for 1 hour, Fig. 2 shows samples. The X-ray diffraction is recorded by "SHIMADZU" XRD -6000 X-ray diffract meter (cukα radiation λ=0.154 nm) in 2θ range from 2º-60º. The distanced d_{hkl} for different planes and average crystallitesize are measured using Eqs. (1), (2).

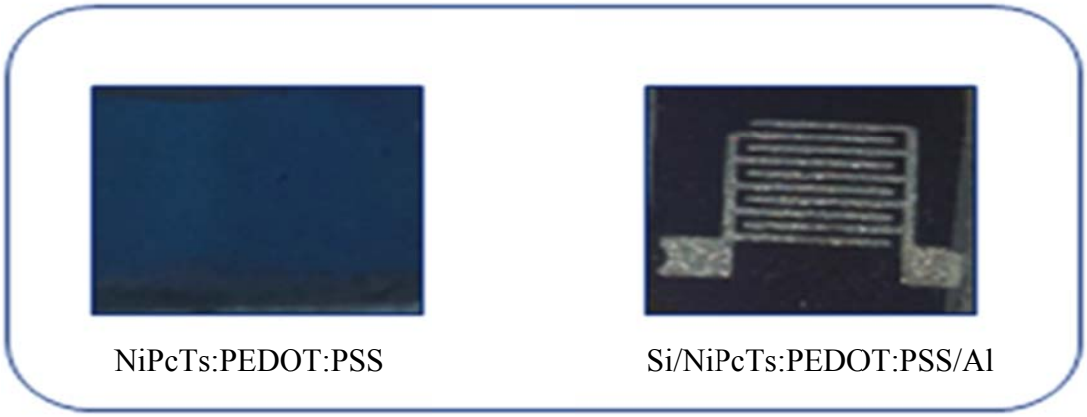

Fig. 2: Samples of NiPcTs: PEDOT:PSS blend.

$$n\lambda=2d\sin\theta \quad (1)$$

λ: wavelength of incident X-ray in angstrom 1.54 Aº, d:interplanar spacing of crystal in angstrom.
θ: angle between the incident rays and surface of the crystal in degree, n=1,2,3…..

$$\text{Crystallite size}=0.94\,\lambda / \text{FWHM}.\cos\theta \quad (2)$$

The Furrier Transform-Infra Red (FTIR TENSOR 27) (400-4000 cm^{-1}) to find out the nature of the bonds with the compound. The testing of gas sensor is shown in Fig. 3, three main measurement are taken, resistances, response time, recovery time according to Eq. (3, 4 and 5) [8].

$$\text{Sensitivity (S)} = \left| (R_g-R_a)/R_a \right| \times 100\% \quad (3)$$

R_g,R_a are the electrical resistance of the film in air and presence of gas.

$$\text{Response time} = \left| t_{gas(on)} - t_{gas(off)} \right| \times 0.9 \quad (4)$$

$$\text{Recovery time} = \left| t_{gas(off)} - t_{gas(recovery)} \right| \times 0.9 \quad (5)$$

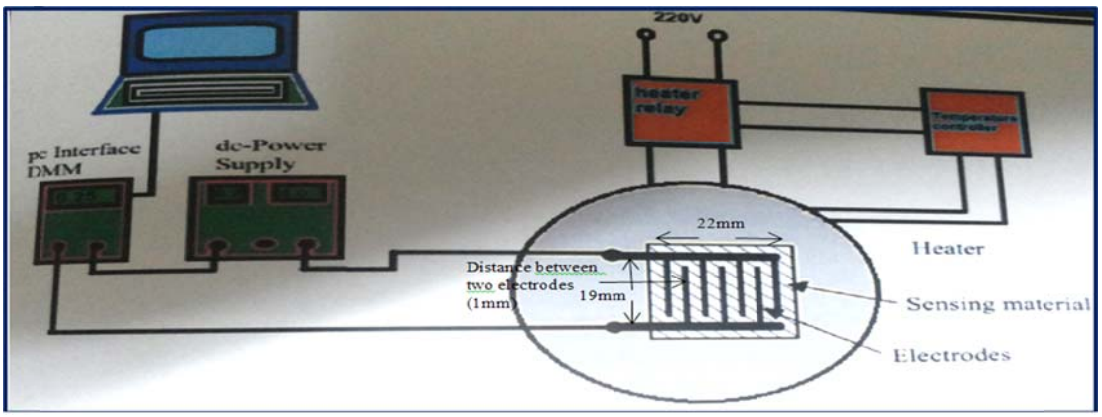

Fig. 3: Schematic diagram of gas sensor testing.

Results and discussion

X-ray diffraction

The X-ray diffraction of the NiPc powder used as the source material for sublimation the peaks are identified using the standard JCPDS File No. 11-0744 data. The FullWidth at Half Maximum (FWHM), d-spacing and grain size were calculated as listed in Table 1.

Table 1: Structural parameters viz. inter-planar spacing and crystalline size of pure NiPcTs powder.

2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	phase	hkl
7.0350	0.380	12.5551	21.0	12.5000	NiPc	(100)
9.1400	0.660	9.6678	12.1	9.7900	NiPc	$(\bar{1}02)$
10.5700	0.750	8.3628	10.6	8.4500	NiPc	(002)
18.0500	0.580	4.9106	13.9	4.9100	NiPc	$(\bar{2}04)$
21.6500	0.780	4.1015	10.4	4.1000	NiPc	(111)
26.8100	0.670	3.3227	12.2	3.3900	NiPc	$(\bar{2}14)$

The structure of NiPcTs powder was determined which gives a polycrystalline structure, monoclinic phase. The spectrum of the NiPcTs powder has shown sharp peaks at reflection surfaces (100), (102), (002), (204), (111) and (214). the peaks simulated by XPowder program to calculate the experimental values of FWHM and grain sizes of NiPcTs powder as shown in Fig. 4. Fig. 5 shows the X-ray diffraction patterns of deposit NiPcTS:PEDOT:PSS bulk heterojunctions blend thin films on glass substrates with different (PEDOT:PSS) concentrations shows Polymorphism structure and the simulations of tow peaks appear (100), (102) refers to NiPcTs While amorphous due to PEDOT:PSS and the peak (102) disappeared in XRD pattern of in concentration (2). Table 2 represents the XRD parameters which are obtained from this measurement for as-deposited NiPcTS:PEDOT:PSS thin film and show the grain size is increased with increasing (PEDOT:PSS) concentrations.

Table 2: Structural parameters viz. inter-planar spacing and crystalline size of NiPcTs:PEDOT:PSS bulk heterojunctions blend thin films.

concentrations	2θ (Deg.)	FWHM (Deg.)	dhkl Exp.(Å)	G.S (nm)	dhkl Std. of NiPc (Å)	hkl
0.5	**7.270**	**0.850**	**12.1498**	**9.4**	**12.500**	**(100)**
1	**7.300**	**0.640**	**12.0999**	**12.4**	**12.500**	**(100)**
2	**7.400**	**0.550**	**11.9367**	**14.5**	**12.500**	**(100)**

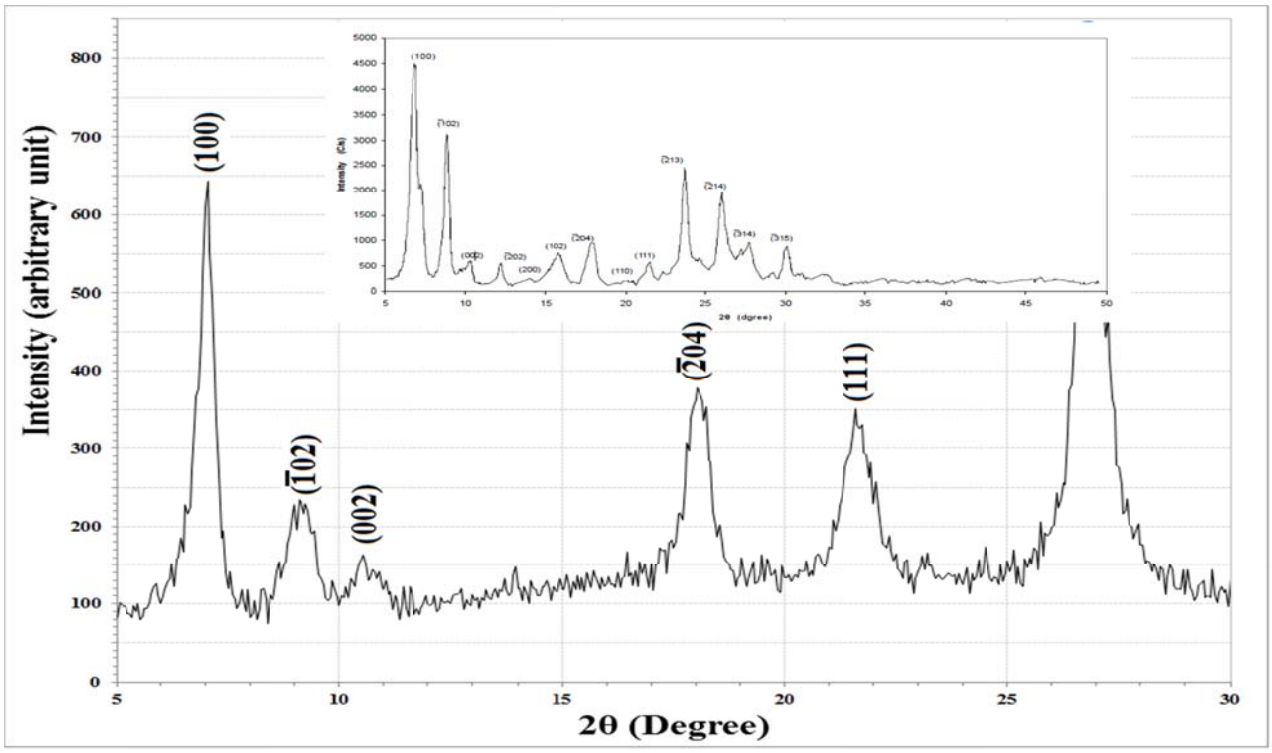

Fig. 4: X-ray diffraction patterns of pure NiPcTs powderas compared with NiPc powder.

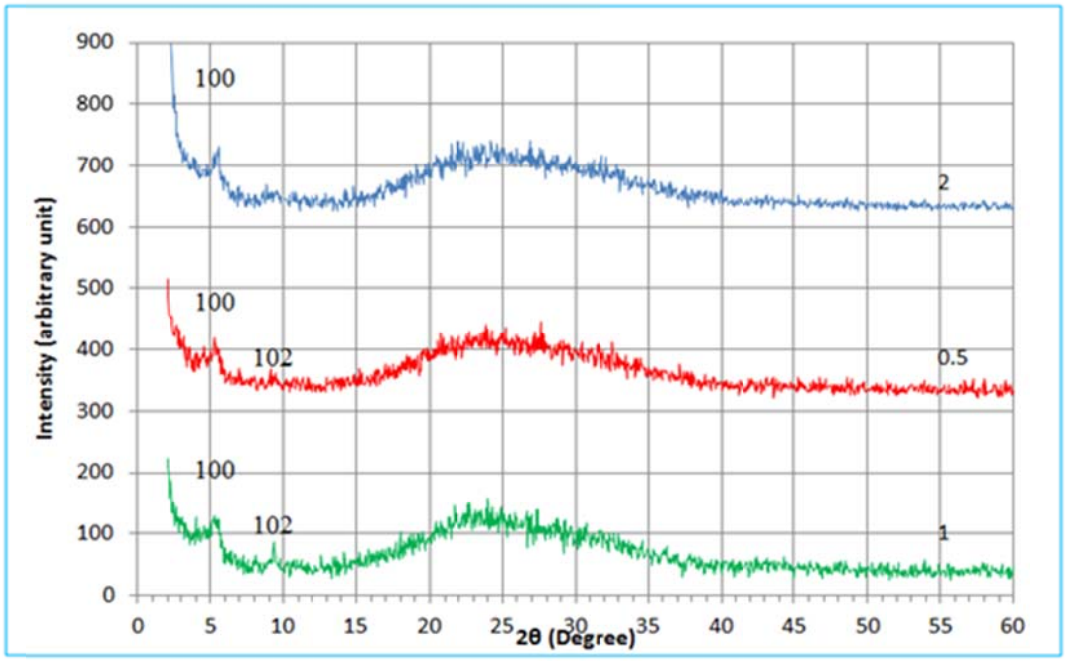

Fig.5: X-ray diffraction patterns of deposit NiPcTS:PEDOT:PSS blend thin films on glass substrates with different (PEDOT:PSS) concentrations.

FT-IR spectrum measurement

Fig. 6 shows the FT-IR spectrum for NiPcTs: PEDOT:PSS bulk heterojunctions blend thin films in different concentration with anneling100ºC for one hour was measured. the NiPcTs : PEDOT:PSS thin films shows the bond bending represented in the range (400-2000) cm^{-1} while the bond stretching represented by the range (2000-4000) cm^{-1}. The spectrum shows a weak peak in the range (600-400) cm^{-1} which indicate the

presence of (metal-Nitrogen) bond vibration at (466-578) cm^{-1} have been assigned for (Nickel – Nitrogen). A number of well-defined bands assigned to PEDOT vibrations are found in the region of 500 to 2000 cm^{-1} as depicted and 1400 to 1500 cm^{-1} associated with C= C symmetrical stretching has been employed to distinguish PEDOT:PSS being in its benzoid and quinoid [19] as shown in Fig. 7. The band at (1400-1100) cm^{-1} is for bond of C-O stretching and the peak (1600-1500) cm-1 indicates C=C bond. The band at (1750-1650) cm^{-1} is for bond of C=O stretching. The band at (2400-2300) cm^{-1} is for bond of C≡C stretching. The band at (2900-2700) cm^{-1} is for bond of C-H stretching. The band at (3500-3400) cm^{-1} is for bond of O-H stretching as shown in Table 3. The spectrum shows the absent of stretching band N-H at band 2358 cm^{-1} which is appears in 0.5 PEDOT:PSS concentration spectrum.

Table 3: The bond of NiPcTs/PEDOT:PSS bulk heterojunctions blend thin films.

Wave number $(cm)^{-1}$	**Bonds Type**
400-2000	Bending
2000-4000	Stretching (weak peak)
600-400	metal-Nitrogen (weak peak)
466-578	Nickel – Nitrogen
1400 - 1500	C= C stretching
1400-1100	C-O stretching
1600-1500	C=C
1650-1750	C=O stretching
2300-2400	C≡C stretching
2700-2900	C-H stretching
3400-3500	O-H stretching

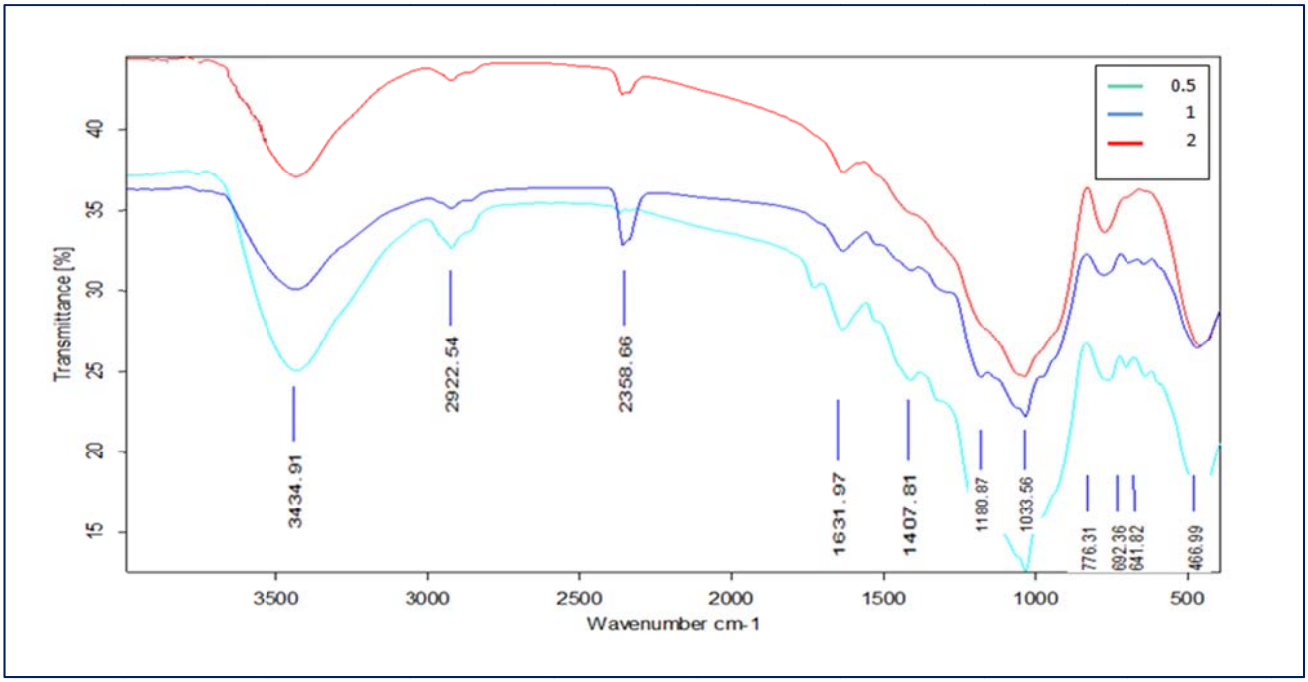

Fig. 6: FT-IR spectra for NiPcTs/ PEDOT:PSS blend thin films of different PEDOT:PSS concentrations.

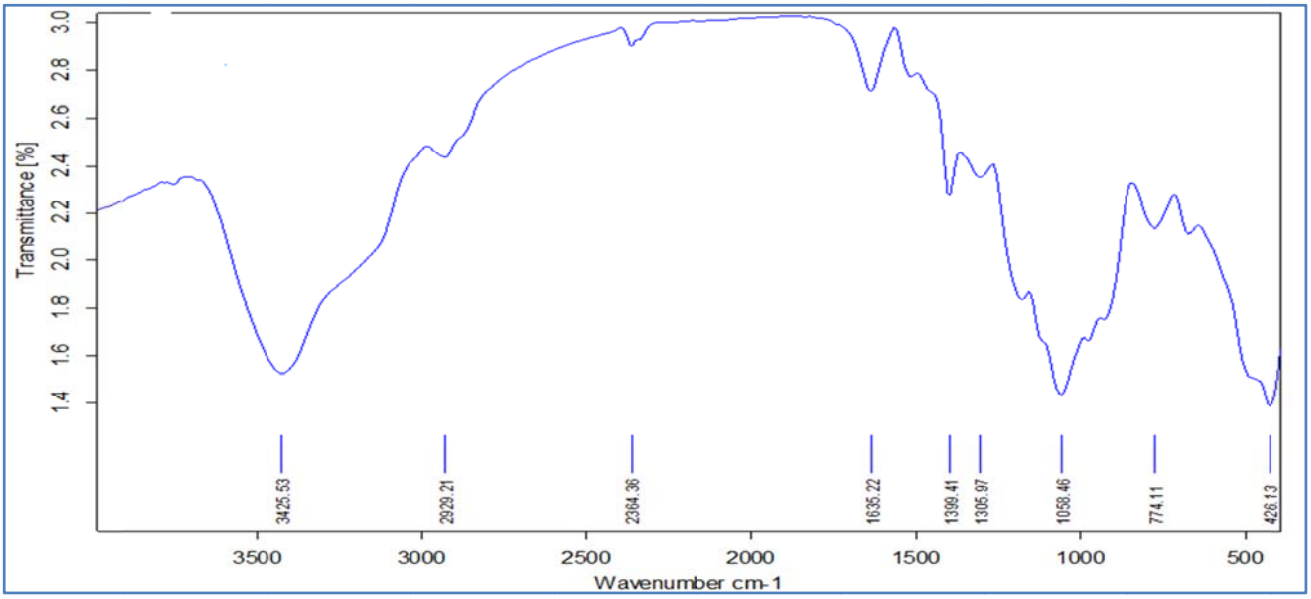

Fig. 7: FT-IR spectra for PEDOT:PSS thin film.

Gas sensor devices

Gas Sensing measurement for Si/NiPcTs/PEDOT:PSS are examined using NO_2,NH_3 gases for different (PEDOT:PSS) concentrations. Fig. 8 show the variation of resistance as function of time with on /off gas value, when the sensor is used to detect the NO_2 gas, the resistance decrease when gas on and the resistance increase when gas off because of the NO_2 is oxiding gas, when the films is p-type the oxygen ions are adsorbed on the surface at grain boundaries and then the charge carriers concentration will be increased, so conductivity is increased. The adsorbed NO_2 gas acts an acceptor in MPc lattice or film. Then, the charge transfer between NO_2 and MPcs occurs and the hole injection after the adsorption extremely enhances the conductivity of MPcs So,

NO_2 gas causes an increase in charge carriers [9]. Found that the gas sensitivities of metallophthalocyanines can be related to the values of their oxidation and reduction potentials [9]. So, the NO_2 gas response of MPcs is depend on the central metal of MPcs, the growth method of the film, the oxidation and reduction potentials of MPcs, side chain of MPcs, morphology of the film, the adsorption capacity of the film etc [10]. And vice versa in the case of the film exposed to NH_3 gas Fig. 9, the resistance increase when gas on and decrease when gas off because of the NH_3 is reducing gas. Figs. 10 and 11 show that The Sensor is a good sensitivity at room temperature than high temperature for NO_2 gas but good sensitivity at 100ºC for NH_3 gas and good sensitivity for NO_2 gas than NH_3 gas while sensor work more effectively in 0.5 concentration. Fig. 12 shows the relation between the response time and recovery time.

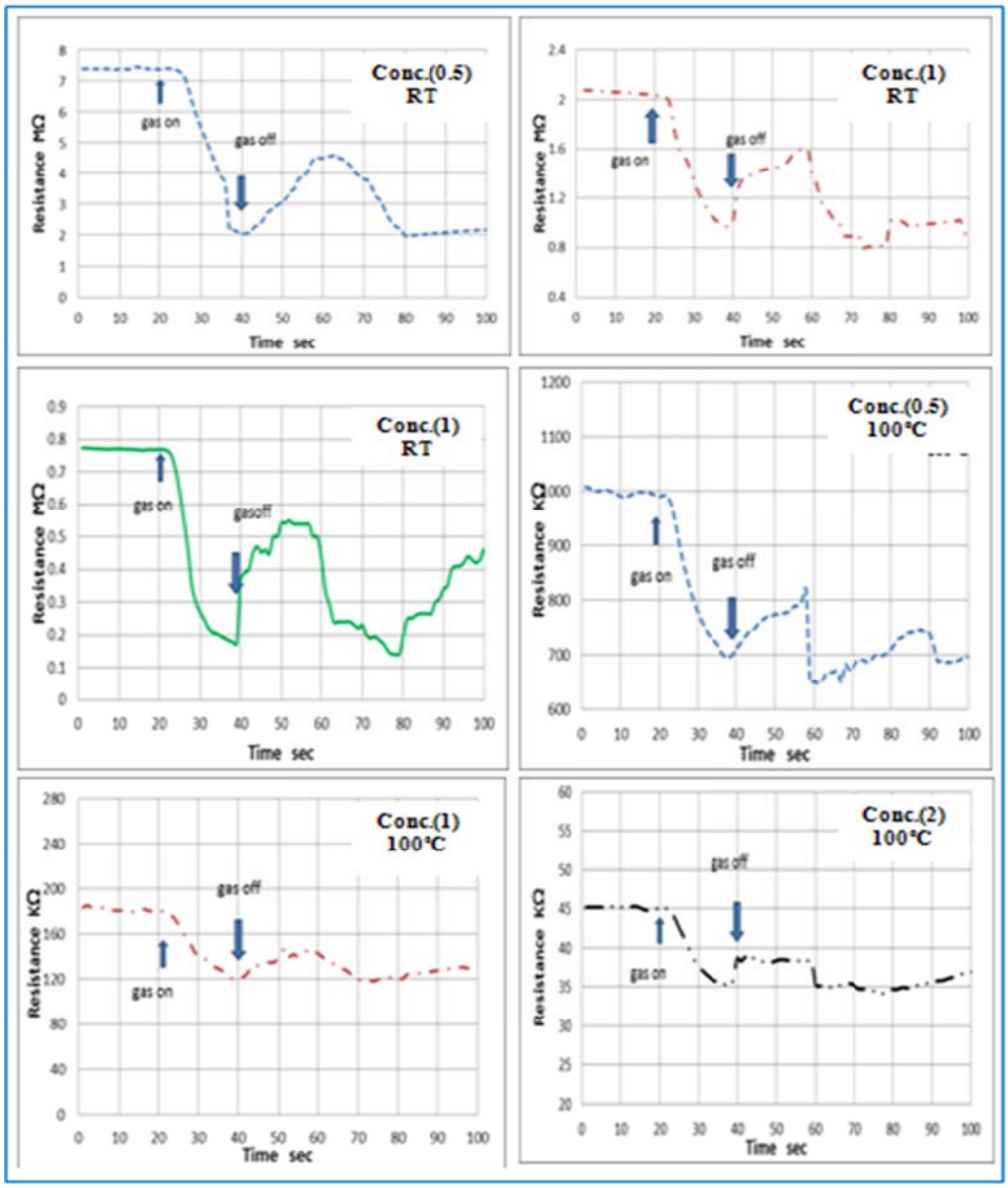

Fig. 8: Resistance as a function of time at different operating temperatures for Si /NiPcTs: PEDOT:PSS bulk heterojunctions blend thin films of different PEDOT:PSS concentrations for NO_2 gas.

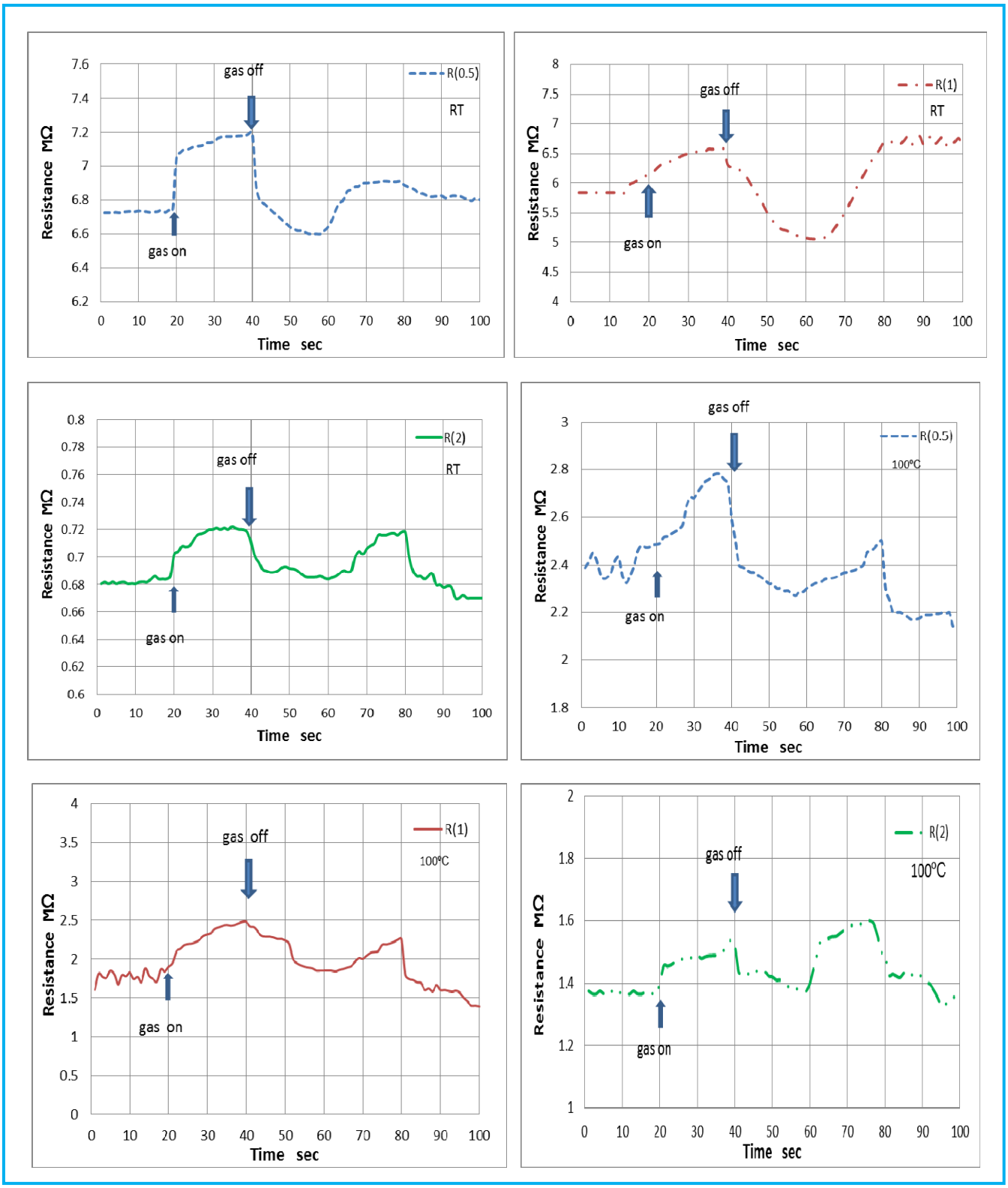

Fig. 9: Resistance as a function of time at different operating temperatures for Si /NiPcTs: PEDOT:PSS bulk heterojunctions blend thin films of different PEDOT:PSS concentrations for NH_3.

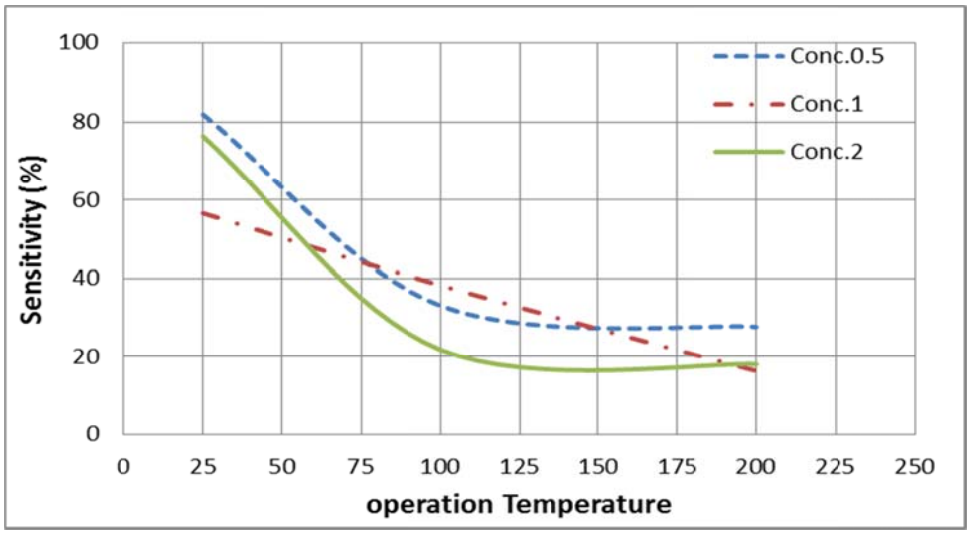

Fig. 10: Sensitivity as a function of operating temperature forSi /NiPcTs/ PEDOT:PSS bulk heterojunctions blend thin films of different PEDOT:PSS concentrations for NO_2 gas.

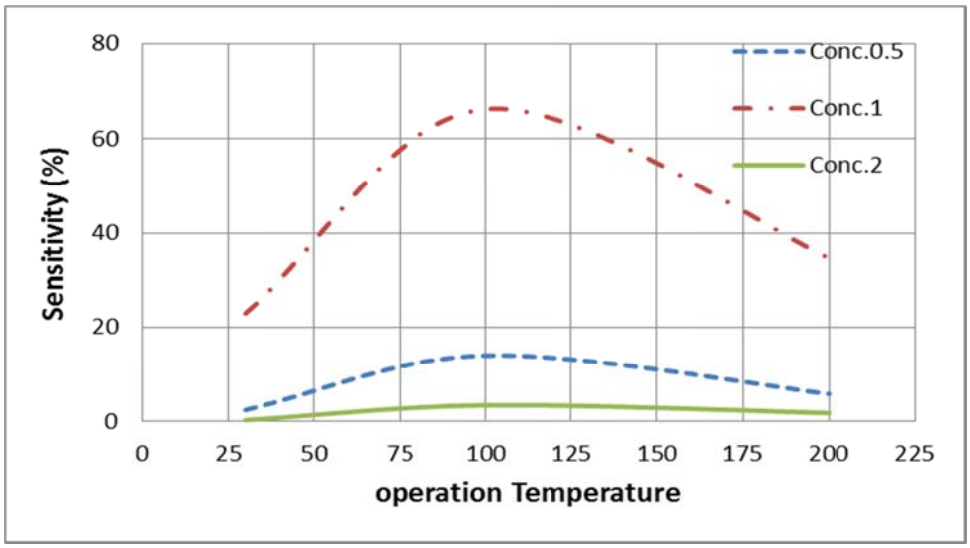

Fig. 11: Sensitivity as a function of operating temperature for Si /NiPcTs/ PEDOT:PSS bulk heterojunctions blend thin films of different PEDOT:PSS concentrations for NH_3 gas.

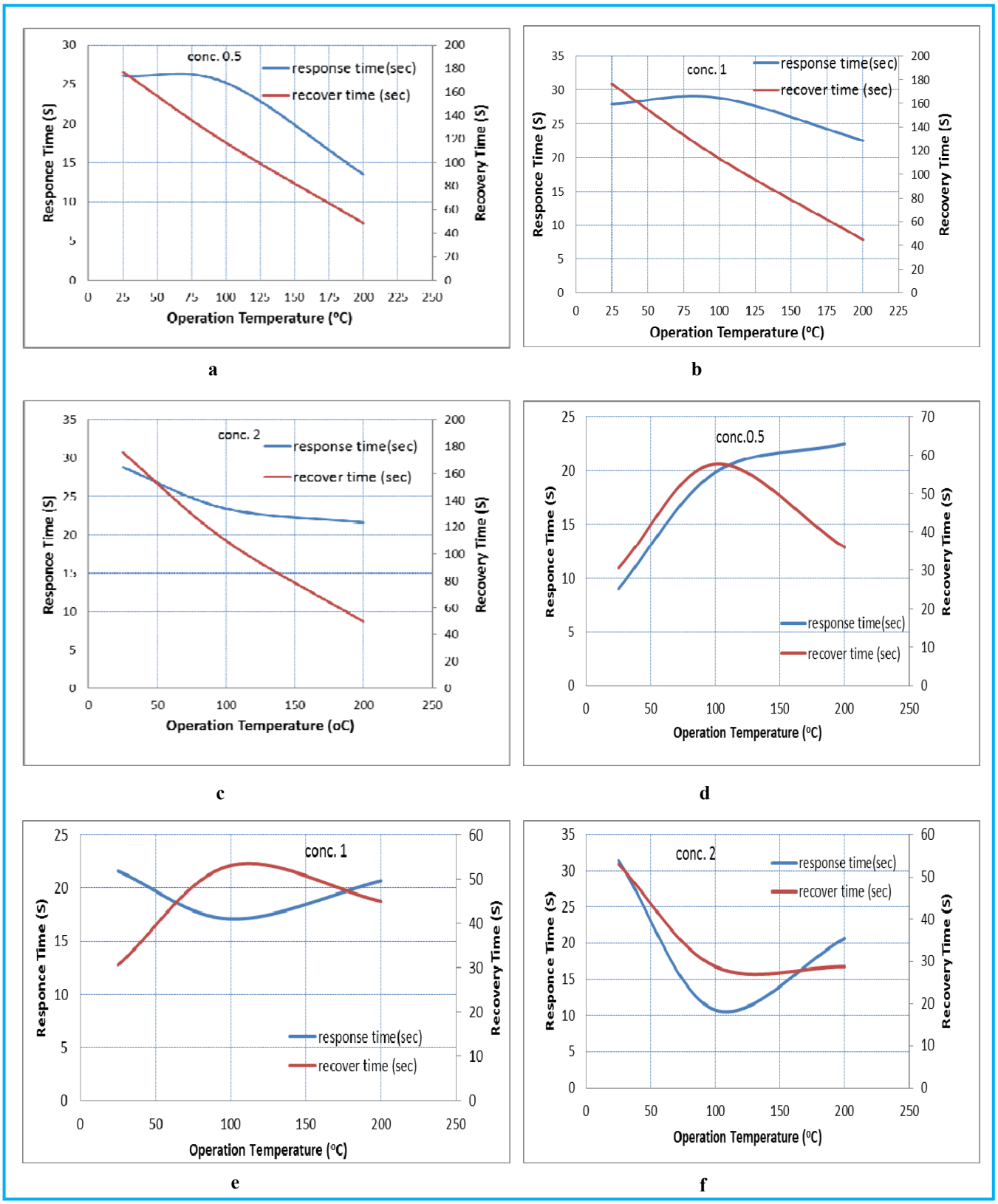

Fig. 12: The variation response time and recovery time with operating temperature for Si/NiPcTs/ PEDOT:PSS bulk heterojunctions blend thin films of different PEDOT:PSS concentrations.(a, b, c) forNO_2 gas and (d, e, f) for NH_3 gas.

Conclusions

The NiPcTS/PEDOT:PSS bulk heterojunctions blend as solution and thin films are successfully prepared by spin coating . XRD analysis of as-deposited (NiPcTs/PEDOT:PSS) with different (PEDOT:PSS) concentrations in dicatedthat the film appeared at(100),(102) in concentrations (0.5, 1) and (100) in concentration (2). The grain size is increased with increasing (PEDOT:PSS) concentrations FTIR measurement was applied to know the type of the bonds of NiPcTS/PEDOT:PSS blend thin films. Gas Sensing measurement for Si/NiPcTs:PEDOT:PSS shows that the NO_2 is oxiding gas and NH_3 is reducing gas. The Sensor show good sensitivity at room temperature than high temperature for NO_2 gas but good sensitivity at 100 ºC for NH_3 gas, and good sensitivity for NO_2 gas than NH_3 gas while sensor work more effectively in 0.5 concentration.

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