

## Investigation of Electrical and Optical Characteristics of Nanohybride Composite (Polyvinyl Alcohol / Nickel Oxide)

A. Hayati, A. Bahari\*

*Department of Physics, University of Mazandaran, Babolsar, Iran*

### Article history:

Received 22/1/2014

Accepted 18/2/2014

Published online 1/3/2014

### Keywords:

OFET

Nano hybride composite

NiO/PVA

Sol-gel method

### \*Corresponding author:

E-mail address:

a.bahari @umz.ac.ir

Phone: 98 9112537702

Fax: +98 1125342480

### Abstract

Some issues; leakage, tunneling currents, boron diffusion are threatening SiO<sub>2</sub> to be used as a good gate dielectric for the future of the CMOS (complementary metal- oxide- semiconductor) transistors. For finding an alternative and novel gate dielectric, the NiO (Nickel oxide) and PVA (polyvinyl alcohol) nano powders were synthesized with the sol-gel method and their nano structural properties were studied using the X-ray diffraction (XRD), Atomic force microscopy (AFM), Scanning electron microscopy (SEM), UV-Vis spectrophotometer and GPS 132 techniques. The obtained results indicated that the sample (5 g NiO and 0.02g PVA prepared at 30°C, annealed in an oven at a temperature of 80°C) can fill this gap due to its higher dielectric constant, better morphology, less rough surface and less leakage current.

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## 1. Introduction

Shrinking electronic devices, in particular gate dielectric thickness down to nano scale range has faced a number of problems, such as increasing leakage, tunneling currents and boron diffusion through the gate dielectric [1-7]. A number of individuals [8-15] have studied many materials to replace silicon dioxide as possible gate dielectrics material. However, none of them could fill this gap and be as a possible gate dielectric of the next transistor generation.

Nickel oxide (NiO), as a possible alternative material, has proven to be an excellent material due to

the different effects in terms of volume, surface, quantum size and quantum tunneling [16,17]. Thus, nano-sized NiO particles are expected to possess many improved properties over those of bulk and micrometer-sized particles. On the other hand, polyvinyl alcohol (PVA) has excellent film forming in addition to emulsifying and adhesive properties. It also has high tensile strength and flexibility [18].

We have thus synthesized PVA/NiO composites with different PVA portions; sample I: 5 g NiO and 0.01g PVA, sample II: 5 g NiO and 0.02g PVA and sample III: 5 g NiO and 0.04g PVA. Their electrical and optical properties have been studied with using

XRD (X ray diffraction), AFM (Atomic force microscopy), SEM (Scanning electron microscopy), GPS132A techniques and a UV-Vis spectrometer. The results indicated that sample II ( 5 g NiO and 0.02g PVA), prepared at room temperature of 30°C, annealed in an oven at a temperature of 80°C, has higher dielectric constant, better morphology, less surface roughness, and less leakage current.

In parallel to above studies, the optical absorption characteristics were also studied by UV-Vis Spectrophotometer to find the band gap energy ( $E_g$ ) with plotting absorbance curve. Results show that, when we added 0.04 g PVA into NiO matrix, (sample III), band gap energy related to NiO nano particles reduced, and the nearly-transparent nature of the samples was revealed in the visible region.

Finally, the obtained results demonstrated that sample II can be considered as a good gate dielectric for the future of OFET (Organic Field effect Transistor) devices.

## 2. Experimental procedure

The NiO/PVA composites were synthesized with the sol-gel method and studied with XRD, AFM, SEM and UV- Vis techniques (See tables 1 and 2 for knowing instruments and material's purity, Company addresses). Nickel nitrate hexahydrate of molecular weight is 290.81 and Molecular weight of repeat unit PVA is 44.00 g/mol. In this work we use the mass ratio of precursors.

Nickel nitrate hexahydrate [ $Ni(NO_3)_2 \cdot 6H_2O$ ] was used as the metallic precursor for the nano crystallites. Then distilled water was used as a solvent of nickel nitrate hexahydrate and PVA polymer. 5g nickel nitrate hexahydrate was dissolved in 50mL of distilled water for 20 min under stirring at room temperature. 0.6 g sodium hydroxide was added to the above solution to adjust the PH value from 10-7. In the other container, 0.01g PVA was dissolved in 50 mL of

water for 20 min under stirring at room temperature. Then the latter solution was added drop wise to the first and was stirred at room temperature.

**Table 1.** Technique applied in detail.

Technique	Country	Company
XRD	Germany	Pillips pw-1710
AFM	Denmark	DME-SPM
SEM	Japan	Hitachi S-4160
GPS 132 A	China	132 A
UV-Vis	China	T80+ UV/vis

The green resultant sol was stirred continuously for 24h. The stabilized sol then changed to gel. The gel was dried in an oven at 80 °C for 24 h and finally a polymeric precursor was gained. In the end, it was milled and powdered. This experiment was repeated with the same procedure for the other sample, as well.

Crystal phases of the nano crystallites were identified by XRD analysis. Microscopy analysis and surface morphology were performed through using AFM and SEM techniques. For electrical properties, we provided a wafer of NiO and PVA/NiO nano powder, and measured the capacity of samples (C) using GPS 132 A. The optical absorption properties were also studied with using UV-Vis Spectrometer.

**Table 2.** Material purchase detail; purity and instruments

Material	Purity	Company
$Ni(NO_3)_2 \cdot 6H_2O$	<98%	AppliChem(USA)
PVA	<98%	Merk(Germany)

## 3. Results and discussion

The crystalline phases were labeled with the index miller and the size of the nano crystallites was

determined using the XRD technique and X-powder software, respectively. As one can see in Fig.1, the two dominated peaks are attributed to NiO(111) and NiO(200) phases [19].

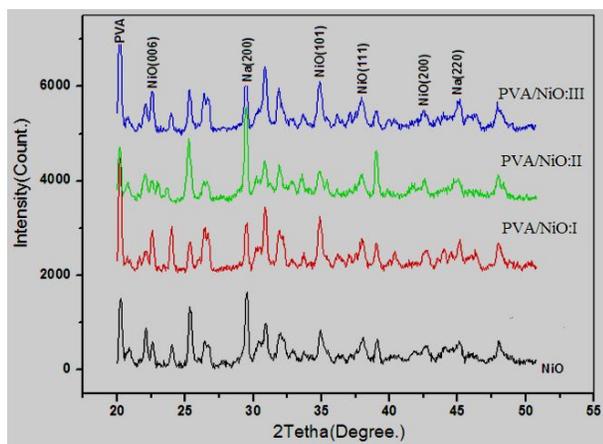
By increasing the content of PVA in powder mixture, no changes occur in NiO phases, but from XRD patterns, it is observed that peaks' intensity related to NiO(111) and NiO(200) phases slightly changed.

The average grain size can be deduced from the Scherer equation [20] and X- Powder software (as examples see Fig.2).

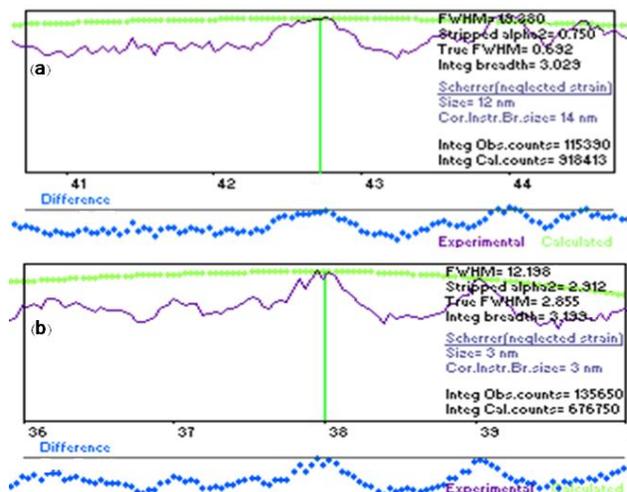
$$D = \frac{k \lambda}{\beta \cos \theta} \tag{1}$$

Where D is the crystallite size of PVA/NiO, K is a constant (0.94),  $\lambda$  is the wavelength of X-ray ( $Cu_{k\alpha}=1.5406 \text{ \AA}$ ),  $\beta$  is true half-peak width, and  $\theta$  is the half diffraction angle of the center of the peak in degree.

According to the Scherer equation and X-Powder software, the size of nano particle related to NiO(200) and NiO(111) phases are determined (Table 2).



**Fig. 1.** XRD pattern of NiO and PVA/NiO nano hybride composite with different contents of PVA.



**Fig. 2.** The size of nano particles correspond with Fig. 1,(a) related to NiO(200) phase and (b) related to NiO(111) phase, are determined with using X- Powder soft ware.

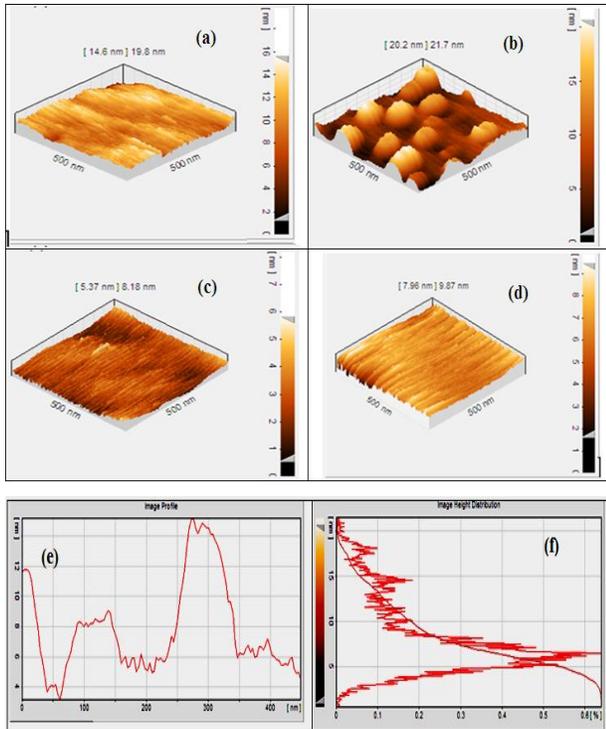
According to Table 3, the size of NiO(111) phase of nanoparticles increases with adding PVA portion (from 3 nm to 6 nm), whilst it is not a regular behavior for NiO(200) phase. The huge peak is found for sample II – NiO (200). The reason could be due to enhancement of electrical dipole arrangement in this case. There are some other lower intensity peaks which are not discussed in the present work, because they can attribute to surface plasmon, interband transitions and impurity which need the other techniques such as low energy electron spectroscopy technique.

One of the main factor for unsuccessful metallic oxide as gate dielectric materials is lower carrier mobility in these materials and also forming an intermediate layer between substrate and metallic film. For this purpose, we study the carrier mobility of nano particles and/or nano crystallites with using DME-SPM technique and analyzed the topography spectra and AFM images (Fig.3). As reported in Refs. [21-23], surface roughness, meaning a number of well- barriers, which act as carrier traps, can affect carrier mobility.

**Table 3.** The size of nanoparticles NiO, PVA/NiO calculated with Scherer equation and X-Powder software.

Sample	Size(nm) 2 $\theta$ =38 $^\circ$	Sample	Size(nm) 2 $\theta$ =43 $^\circ$
NiO(111)	5	NiO(200)	8
I	3	I	12
II	4	II	27
III	6	III	8

As measurement data with DME- SPM technique (Table 4) show sample II has a surface with lower  $S_a$ ,  $S_y$ , meaning that, it has a partly flat and smooth surface morphology and therefore higher carrier mobility as well as better electric current output.



**Fig. 3.** AFM images (3-D) of sample (a) NiO, (b) I, (c) II and (d) III. (e) Topography spectrum as an example for sample II. (f) Particle's distribution spectrum and fitting line for sample II.

**Table 4.** Roughness factors of NiO, NiO/PVA samples obtained through DME-SPM software.

Sample	$S_y$ (nm)	$S_m$ (nm)	$S_a$ (nm)	$S_q$ (nm)
NiO	6.45	5.75	0.91	1.12
I	8.46	7.26	1.24	1.53
II	5.89	3.72	1.03	1.28
III	21.11	18.31	3.16	3.93

Moreover, island-shaped morphologies on the sample I in Fig. 3(b) indicates that the particles come close to each other to form an agglomeration surface structure with many grains, and visible crystallites contours due to increment of polarons in sample I surface [21].

The Roughness Average ( $S_a$ ), Mean Value ( $S_m$ ) and Root Mean Square ( $S_q$ ) calculated from the data, are defined with the following formula:

$$S_a = \frac{1}{N} \sum_{l=0}^{N-1} |z(x_l)|$$

$$S_m = \frac{1}{N} \sum_{l=0}^{N-1} z(x_l)$$

$$S_q = \sqrt{\frac{1}{N} \sum_{l=0}^{N-1} (z(x_l))^2}$$
(2)

Figures 4 and 5 show the SEM images of the NiO and PVA/NiO samples. Figure 4(b) exhibits that agglomeration surface structure with many grains in close agreement with the AFM image (see Fig. 3(b)) reaches to a point where adding PVA content in PVA/NiO nano hybrid composite could increase to 0.04 g ( sample II ) , and get a more smooth surface with minimum roughness compared to the other present samples. The surface roughness clearly helps increase the disorder, and affects the uniform growth of the semiconductor [23], and also dielectric roughness is believed to reduce mobility in organic semiconductors due to the disorder induced in the accumulation layer [21,22]. It means that the number

of trapping of charge carrier decreases. It causes an enhancement of carrier's mobility ( $\mu$ ) with reducing the trap site. In agreement with formula

$\sigma = q (n \mu_e + p \mu_p)$  Conductivity increases with the mobility, too. In this formula  $\sigma$  is conductivity,  $q$  is the charge of electron and hole carriers,  $n$  and  $p$  are the density of carriers and  $\mu_e$  and  $\mu_p$  are the mobility of electrons and holes respectively.

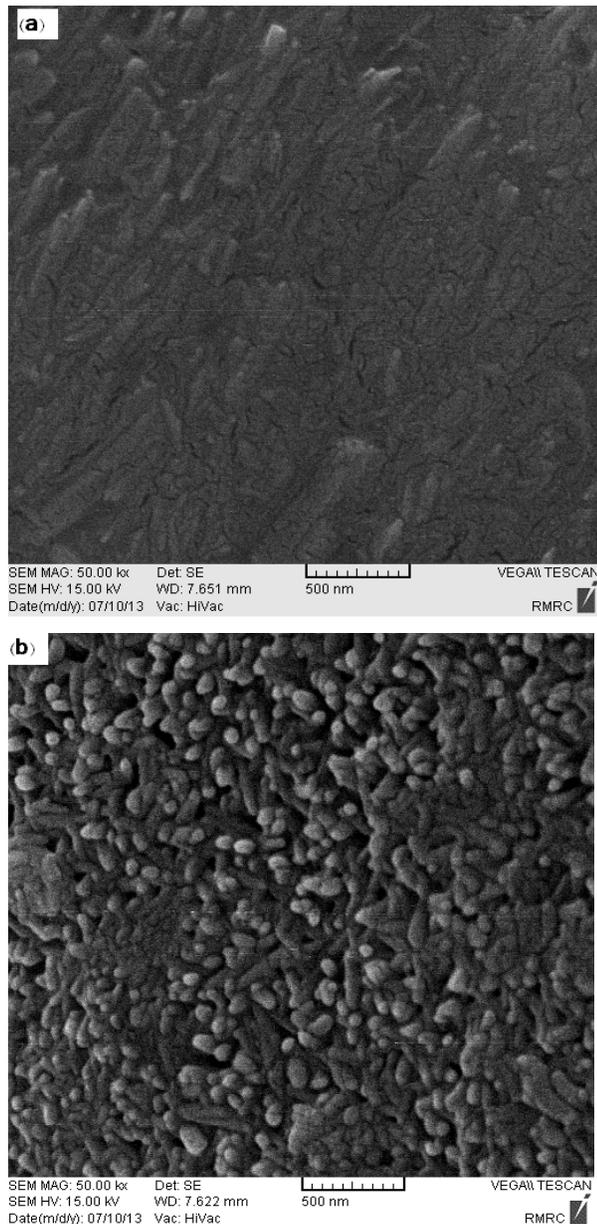


Fig. 4. SEM images of samples: (a) NiO and (b) I.

It was expected that the PVA/NiO nano hybride composite with tight surface, would have good blocking function to prevent the growth of SiO<sub>2</sub> interface in MOSFETs (Metal-oxide-semiconductor field effect transistor) [22].

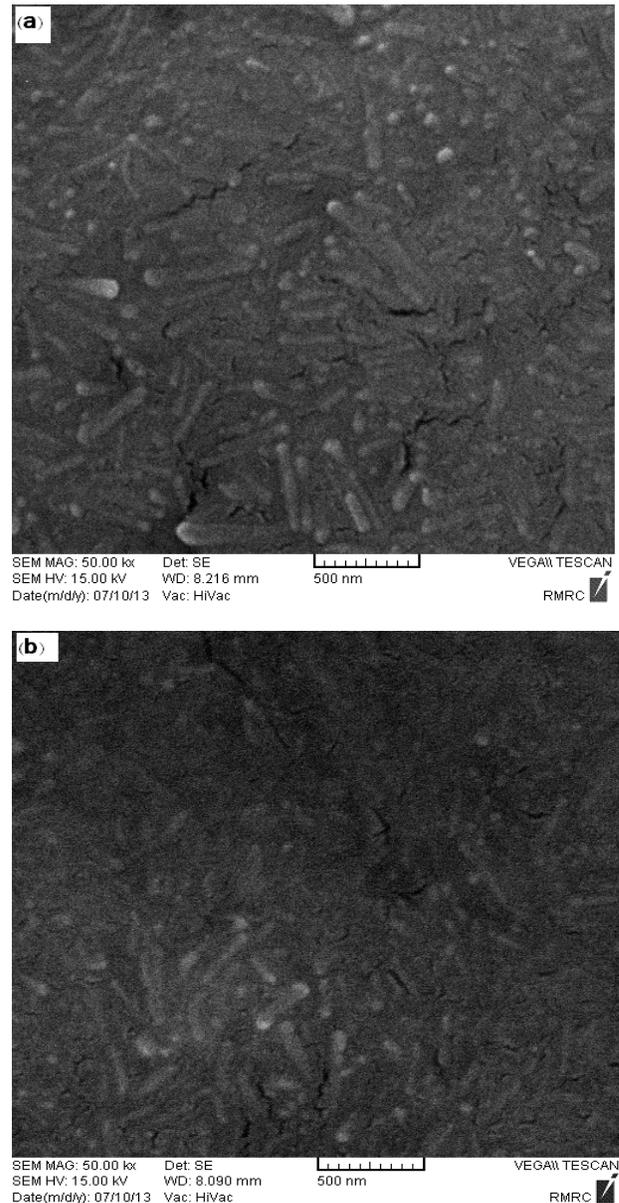


Fig. 5. SEM images of samples: (a) II and (b) III.

For studying electrical property of PVA/NiO nano powder, we made capacitors with NiO and PVA/NiO nano powders and measured capacity of samples, with

using GPS 132 A technique and determined dielectric constant (k) for the samples with considering basic formula;  $k = \frac{cd}{\epsilon_0 A}$

In this formula  $d=3\text{mm}$ ,  $A=1.13\text{cm}^2$  and  $\epsilon_0= 8.85 \times 10^{-12} \text{C}^2 / \text{Nm}^2$ . Dielectric constant and the other physical characteristic of samples are determined with GPS 132 A and the measurement data are gives in Table 5. The obtained results presented in Table 5 indicate quality factor ( $Q_F$ ), dissipation factor ( $D_F$ ), resistance (R), capacitance (C) and dielectric constant (K).

**Table 5.**  $Q_F$ ,  $D_F$ , R, C and K of PVA/NiO samples (S) obtained with using GPS 132 A (with  $A = 1.13 \text{ cm}^2$  and thickness =3 mm)

s	$Q_F$	$D_F$	R (MΩ)	C (PF)	K
I	0.94	1.03	6.44	173.5	52
II	0.98	1.07	0.92	3.35	56
III	0.45	2.2	1.53	9.70	29

Higher  $Q_F$  value indicates a lower rate of energy loss, compared to the stored energy of the capacitor as demonstrated in Eq. (3):

$$Q_F = 2\pi \times \frac{\text{Energy stored}}{\text{energy dissipated per cycle}} \quad (3)$$

The  $D_F$  value defined with Eq. (4) gives the loss-rate of energy of capacitor and varies with the dielectric material and decreases at higher temperature.

$$D_F = \frac{1}{Q_F} \quad (4)$$

Mathematically, the expression for current density according to the Poole-Frenkel model can be written as [24];

$$j = AT^2 \exp \frac{1}{K_B T} \left[ \left( \frac{57.7eV}{kd} \right)^{1/2} - \phi \right] \quad (5)$$

Where k is the dielectric constant of the sample, d is electrode spacing in Å,  $\phi$  is the depth of the trap potential well and A (Richardson constant) is  $120 \text{ A/cm}^2\text{k}^2$ . The obtained results show that the sample II has highvalue of dielectric constant ( $k=56$ ) compared to the others (Table 5).

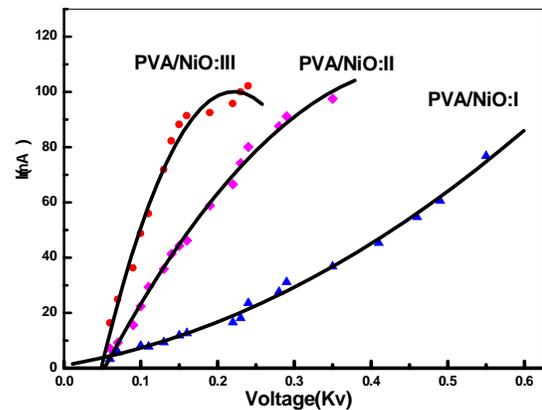
Figure 6 shows the I-V curves of sample I, II and III. The fitting of the I-V curves shows a sextic function behavior given by:

$$I = aV^6 + bV^5 + cV^4 + dV^3 + eV^2 + fV + g \quad (6)$$

Coefficients a, b, c, d, e, f and g have been specified in Table 6.

**Table 6.** Sextic function coefficients ( $\times 10^4$ ) for PVA/NiO samples

Sample	a	b	c	d	e	f
I	-1122	852.5	-	30.8	-1.9	0
II	38304	-	3825	-364	17	0
III	10204	-	2541	-328	-2.3	0



**Fig.6.** I-V curves of PVA/NiO samples.

Comparison between I-V curves of the samples, it is clear that  $V / I$  is not constant value, as expected

for ohmic contact behavior, whilst, the I-V diagram for sample II is an ohmic contact behavior. In parallel to above studies, optical absorption spectra of the powered samples were recorded in UV-Vis spectrometer and energy gap value was then calculated by Tauc equation (7) [25]:

$$(\alpha h\nu)^{\frac{1}{2}} = C(E - E_o) \tag{7}$$

Where  $h\nu$  is the photon energy,  $C$  is a constant for a direct transition and  $\alpha$  is the optical absorption coefficient, so that

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right) \tag{8}$$

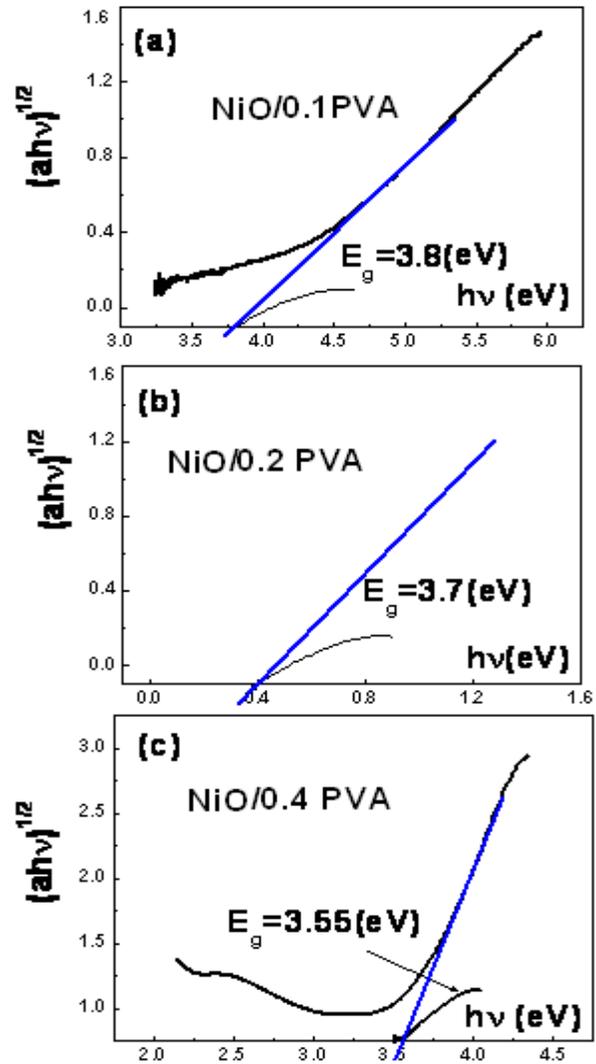
Where  $d$  is the nano crystallites thickness and  $T$  is the optical transmittance.

By looking the optical band gap in Fig.7, we can see that when the amount of PVA in NiO matrix reaches to 0.04 g (sample III), the optical band gap ( $E_g$ ) for direct band gap reduced to lower  $E_g$  (3.55eV). It is worth noting that the value of band gap energy is lower than the energy reported by Z Zhang [26]. Here it is also observed that sample III sample is almost transparent in visible region, as expected from the Mott result.(for more detail see [27]). We summarized the last decade results of some worker with different gate dielectric materials in Table 6.

**Table 6.** R, K, C and gate dielectric thickness reported with some workers and in the present work.

Sample	K	C (pF)	D (nm)	Ref.
TiO <sub>2</sub> /PVA	5.4	-	600	[28]
Ba TiO <sub>2</sub> /PVA	9-12	0.065	170	[29]
SiO <sub>2</sub> /PDDA*	6	-	300	[30]
NiO/PVA	56	3.35	3000	Present work

PDDA\* (Poly diallyldim ethyl ammonium chloride)



**Fig.7.** (a), (b) and (c) U-Spectra of PVA/NiO samples

#### 4. Conclusion

In the present work, the electrical and optical properties of the PVA/NiO nanocrystallites that were prepared by the sol-gel method are studied. XRD analysis reveals that as the PVA content in the nanocrystallites increases, in contrast to peak's intensity, no changes occur in the NiO(111) and NiO(200) phases. It means that adding PVA content in NiO matrix does not affect the nano crystallite phases. On the other hand, the Poole-Frenkel effect, due to the trap levels originated from structure's defects (see AFM images), indicates that the oxygen - nickel - carbon atoms in the samples, in particularly

in the grain boundary regions reduce the carrier mobility as well as change the electrical properties of nanostructural the samples. Since the permittivity value of sample II dielectric, which is higher than that of other present samples, can be transfer much more carriers and yield more current flux in the drain of the OFET transistors due to faster carriers through the channel.

Therefore, sample II with stated properties can be considered as a good gate dielectric material for the next OFET generation.

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