بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

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Improved Photovoltaic Performance of Au Doped NiO/WO3 Films

By

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Introduction

1.Thin Film Techniques

- Thin film techniques are one of the most recent Integrated technologies that greatly contribute for developing the study of semiconductors and providing a clear picture of their physical and chemical properties.

- The thin films a layer or several layers of atoms of a substance whose thickness does not exceed one micron, and since this layer of film is thin, it is deposited on bases of glass, silicon, aluminum, quartz, etc., depending on the desired study or scientific need .

- these films are exploited in many fields, such as integrated circuits, manufacturing crosses (pn), imaging, anti-reflective coatings, modifiers, as well as optical communications including That's solar cells, LED lights, detectors.

2. Materials used in the work

2.1 Nickel Oxide (NiO)

- Among various forms of nickel oxide, nickel monoxide (NiO) is most studied.
- NiO is a good insulator
- NiO takes a cubic structure as its stable form at room temperature
- NiO is a p-type semiconductor material
- It has a wide bandgap of (3.6–4.0) eV at room temperature

Some physical Properties of NiO

Name	Property
Symbol, number	^{28} NiO
Element category	Transition metal
Crystal structure	Face-centered cubic
Molar mass	74.692gm/ mol
Density	6.67gm/cm^3
Melting point	2228 K
Appearance	Green,black
Molecular weight	74.693 g/mol

2.2 Tungsten Oxid (WO_3)

- WO_3 is one of the most interesting materials exhibiting a wide variety of novel properties especially in thin film form useful for advanced technological applications
- The physical properties of a material are greatly affected by its structural order and morphology
- Tungsten oxide films are presently used in sunglasses and automotive rear-view mirrors, sun roofs, variable-tinted windows for automotive glass and building windows

Some physical properties of WO_3

Name	Property
Symbol, number	^{74}WO3
Element category	Transition metal
Crystal structure	Monoclinic
Molar mass	231.84gm/mol
Density	7.16 gm/cm^3
Melting point	1746 K
Appearance	yellow powder
Boiling point	1970 K
Molecular weight	231.84 g/mol

2.3 Gold (Au)

- The optical and spectroscopic properties of Au have been extensively exploited for chemical,bioanalytical, and biomedical applications
- Gold (Au) is specially attractive among nanomaterials as they show vibrant optical absorbance
- Gold isn’t soluble in mineral acids
- Gold is one of the few metallic elements that can be used in nanoscale devices and systems due to its resistance to oxidation

some physical properties of Au

Name	Gold
Symbol, number	^{79}Au
Element category	Transition metal
Crystal structure	Face-centered cubic
Molar mass	196.9665 gm/ mol
Density	19.30 gm/cm^3
Melting point	1337.33 K
Appearance	Metallic yellow
Boiling point	3243 K
Molecular weight	196.966 g/mol

3.The Aim of The Study

The aim of the present work is anhanced the efficiency of solar cell by modifying specific properties of(NiO:WO3) films deposited on Si using PLD technique by doping (NiO:WO3) films with different concentration of Au at different ratios (0.03,0.05,0.07)wt. The main objectives of this work are:

- Initially the series of samples have been prepared by PLD technique at different Au on glass and Si substrates.
- Study the effect of the Au doped with different concentration and annealing process on the structure using XRD,FTIR,and surface topography using AFM in addition to the optical and electrical properties for the deposited films.
- Study the figure of merit of prepared heterojunctions (NiO:WO3) Au/p-Si solar cell.

Experimental Work

Schematic diagram for our experimental work

Preparing of $(NiO_{0.85}:WO_{3\ 0.15})$ pellet

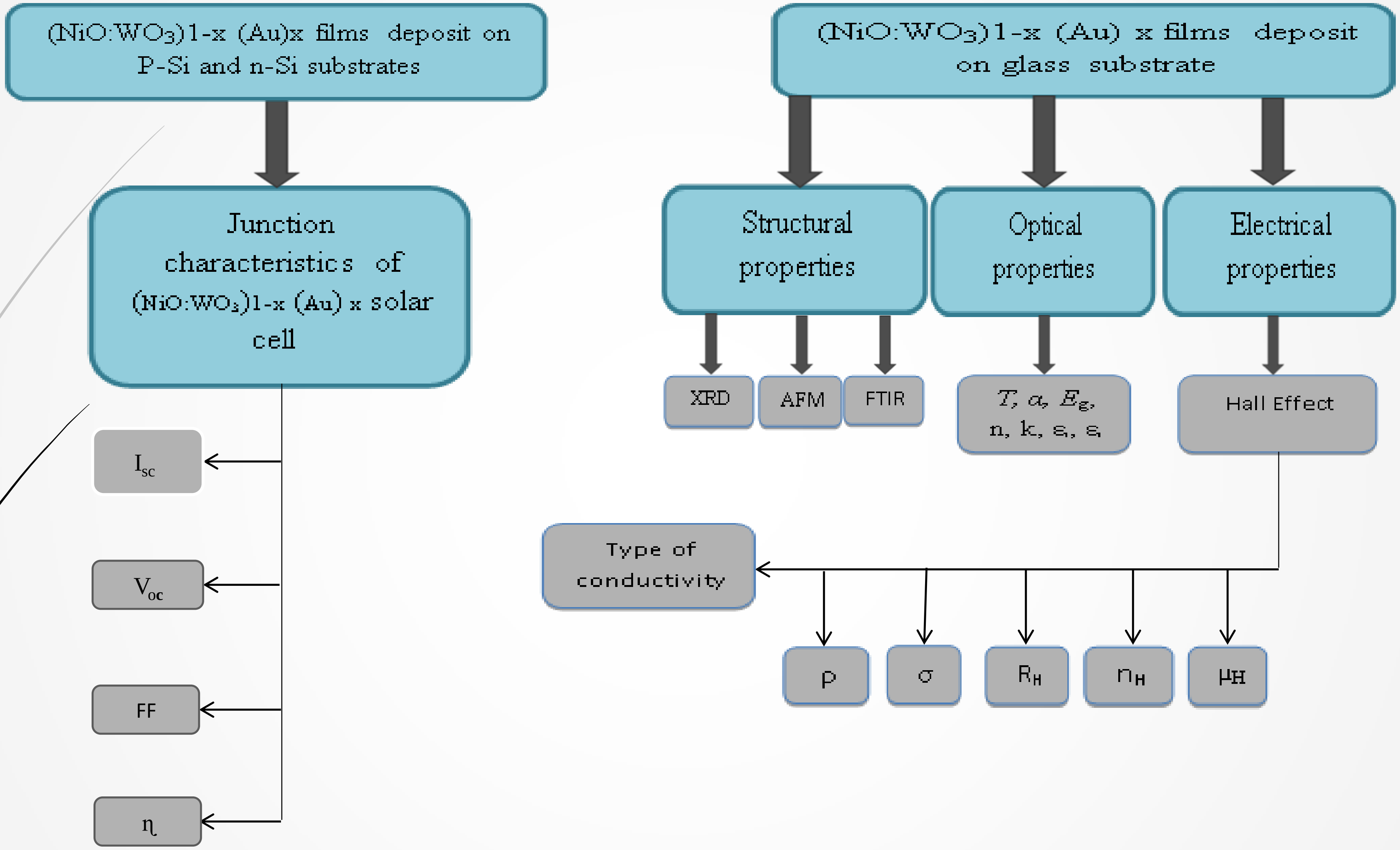
Using hydraulic under pressure (5) tons

Preparing of $(NiO:WO_3)_{1-x}$ $(Au)_x$ pellets at different concentration of x= (0.03,0.05,0.07) wt using hydraulic under pressure (5) tons

Sintering the pellets at temperature 973K for (1) hour

Preparing of $(NiO:WO_3)_{1-x}$ $(Au)_x$ thin films by PLD techuique at RT, No. of pulse (400) & E= (600) mJ

All the films are annealing to temperature 573K for (1) hour



(NiO:WO3)1-x (Au)x films deposit on P-Si and n-Si substrates
Junction characteristics of (NiO:WO3)1-x (Au) x solar cell
I_{sc}
V_{oc}
FF
η
(NiO:WO3)1-x (Au) x films deposit on glass substrate
Structural properties
Optical properties
Electrical properties
XRD
AFM
FTIR
T, α, E_g, n, k, ε, ε
Hall Effect
Type of conductivity
ρ
σ
R_H
n_H
μ_H

Results and Discussion

Structure and Topography properties

X-Ray diffraction

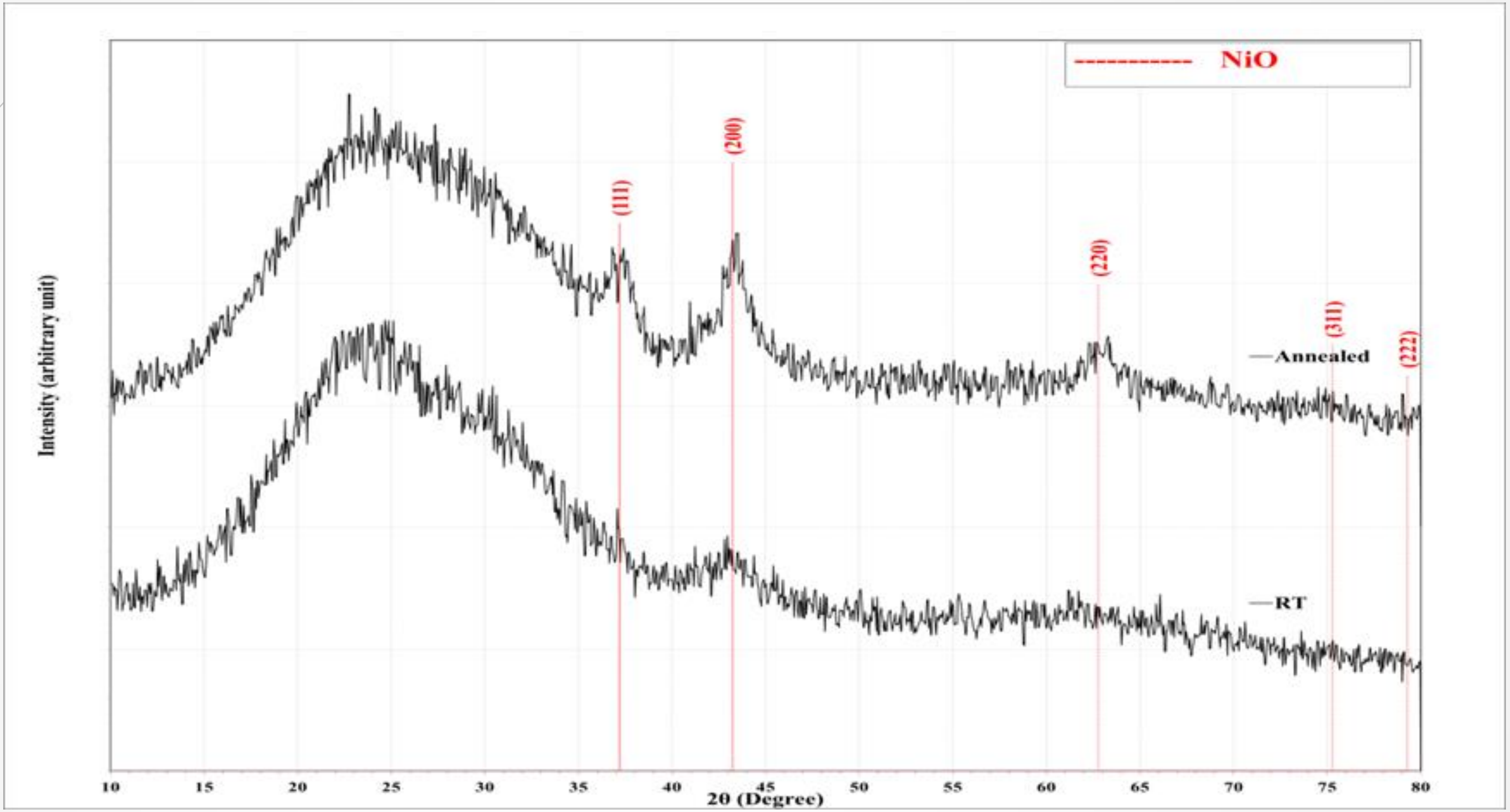


Figure (1): shows the X-ray diffraction of the prepared NiO thin films at room temperature and when annealing to 573K.

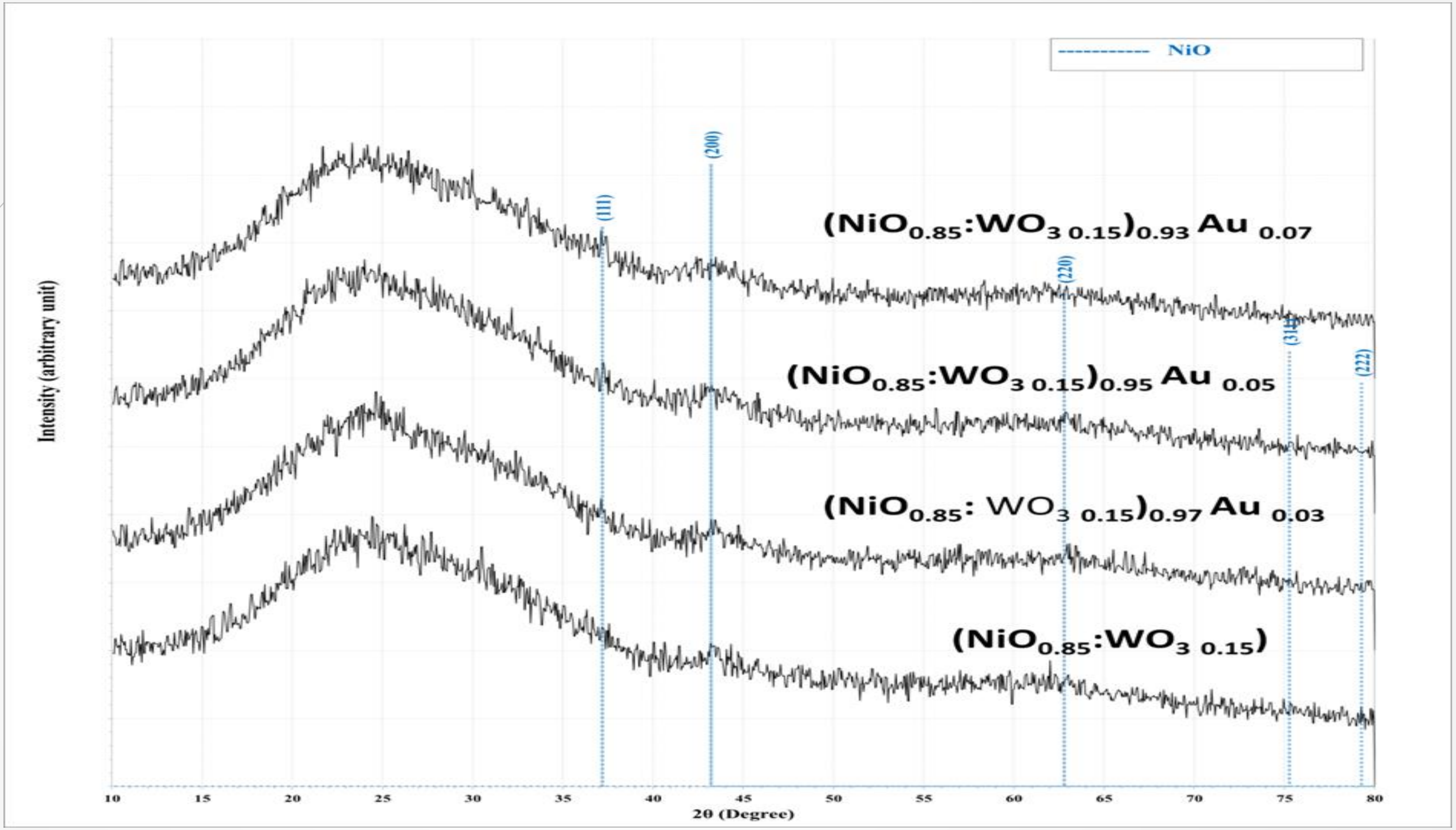


Figure (2): shows the X-ray diffraction of ($NiO:WO_3$) doped with different contents of Au particles at room temperature.

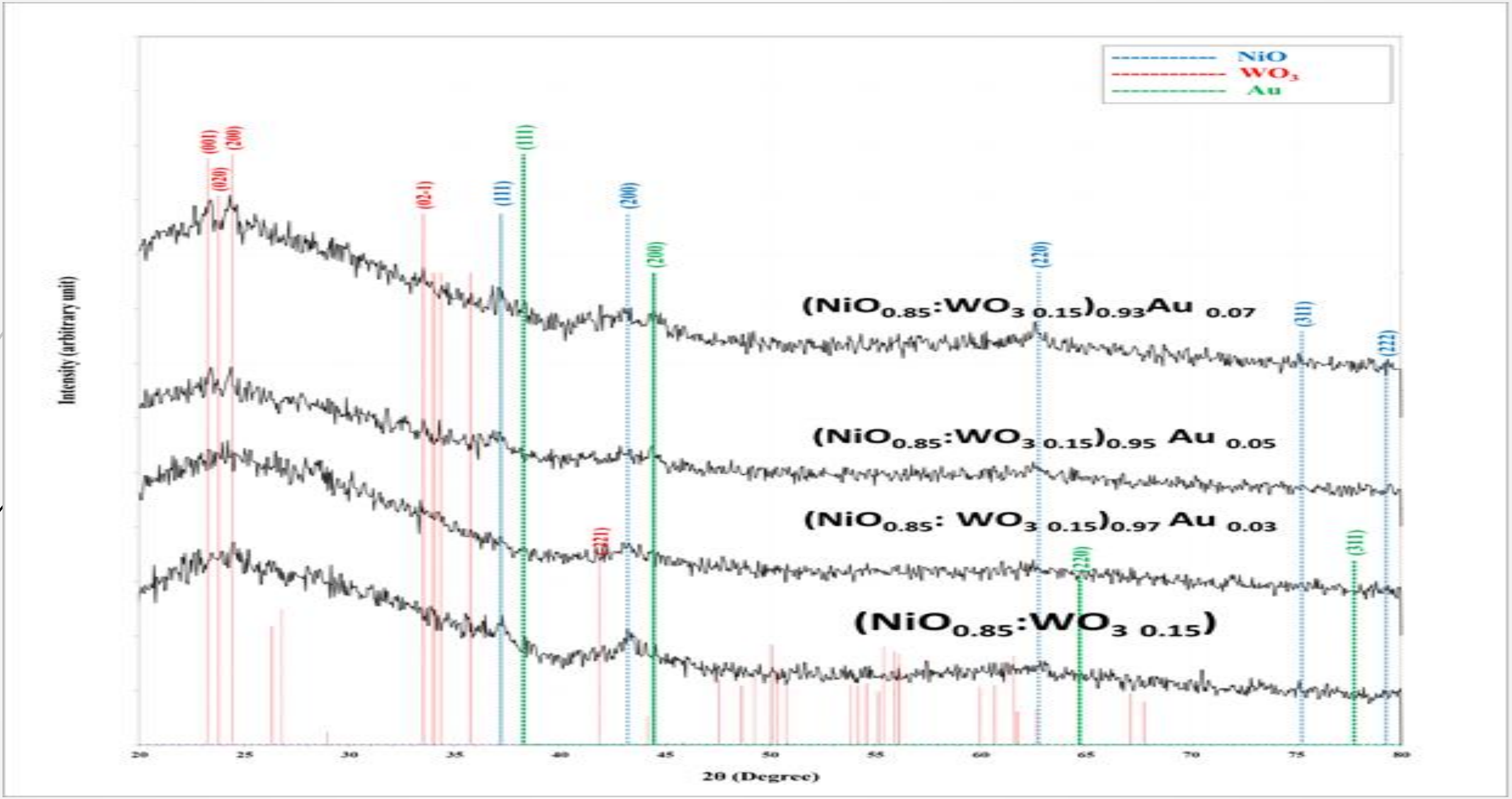


Figure (3-3): shows the X-ray diffraction of (NiO: WO_3) doped with different contents of Au particles when annealing at 573 K.

Atomic Force Microscopy (AFM)

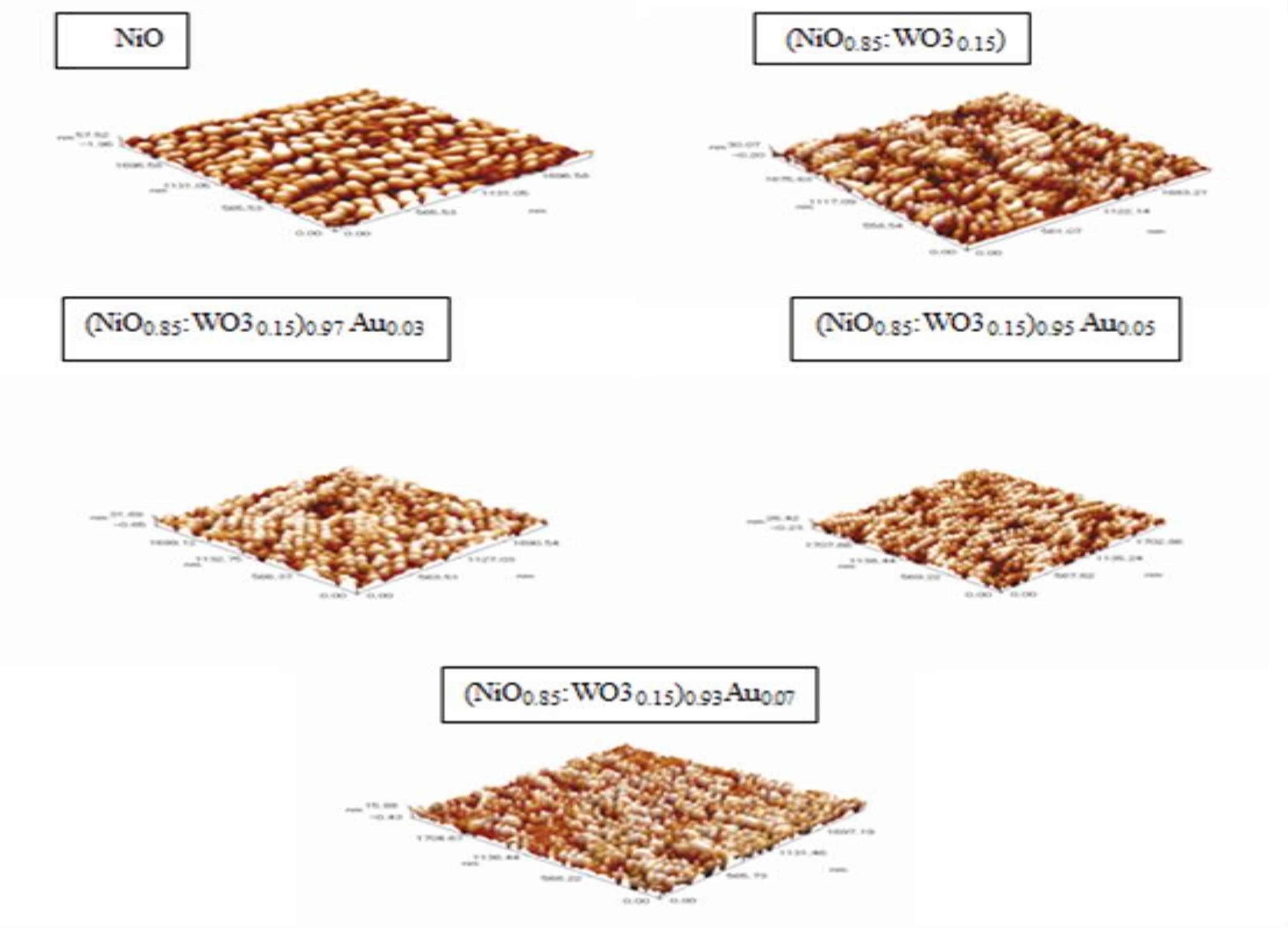


Figure (4): AFM images at room temperature.

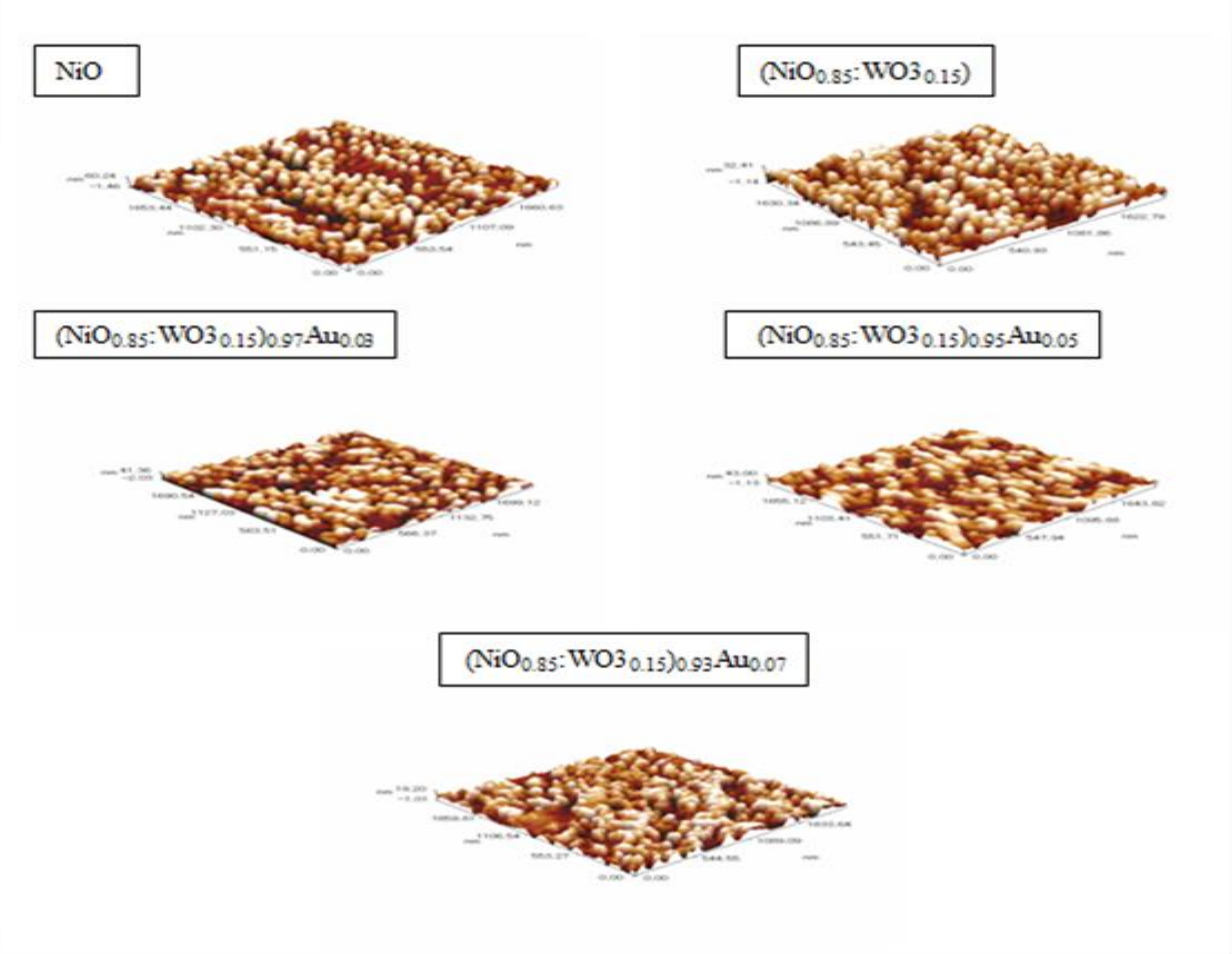


Figure (5): AFM images when annealing at 573 K.

Table: (1)Average of the surface roughness and the granular size for the prepared films before and after annealing according to sample.

Sample	Average Diameter (nm)	Average Roughness (nm)	R.M.S (nm)	Peak-peak (nm)
NiO	82.86	15.4	17.6	59.5
$(NiO_{0.85}:WO_{3\ 0.15})$	59.96	7.57	8.74	30.3
$(NiO_{0.85}: WO_{3\ 0.15})_{0.97}Au_{\ 0.03}$	81.02	7.58	8.9	32.5
$(NiO_{0.85}:WO_{3\ 0.15})_{0.95}Au_{\ 0.05}$	60.92	6.86	7.87	26.6
$(NiO_{0.85}:WO_{3\ 0.15})_{0.93}Au_{\ 0.07}$	56.22	4.1	4.73	16.3
Ta=573 K				
Sample	Average Diameter (nm)	Average Roughness (nm)	R.M.S (nm)	Peak-peak (nm)
NiO	75.47	15.4	17.8	61.7
$(NiO_{0.85}:WO_{3\ 0.15})$	64.81	8.39	9.69	33.6
$(NiO_{0.85}:WO_{3\ 0.15})_{0.97}Au_{\ 0.03}$	83.27	10.9	12.5	43.4
$(NiO_{0.85}:WO_{3\ 0.15})_{0.95}Au_{\ 0.05}$	75.41	9.65	11.2	40.3
$(NiO_{0.85}:WO_{3\ 0.15})_{0.93}Au_{\ 0.07}$	62.47	5.09	5.86	20.2

FT-IR Measurements

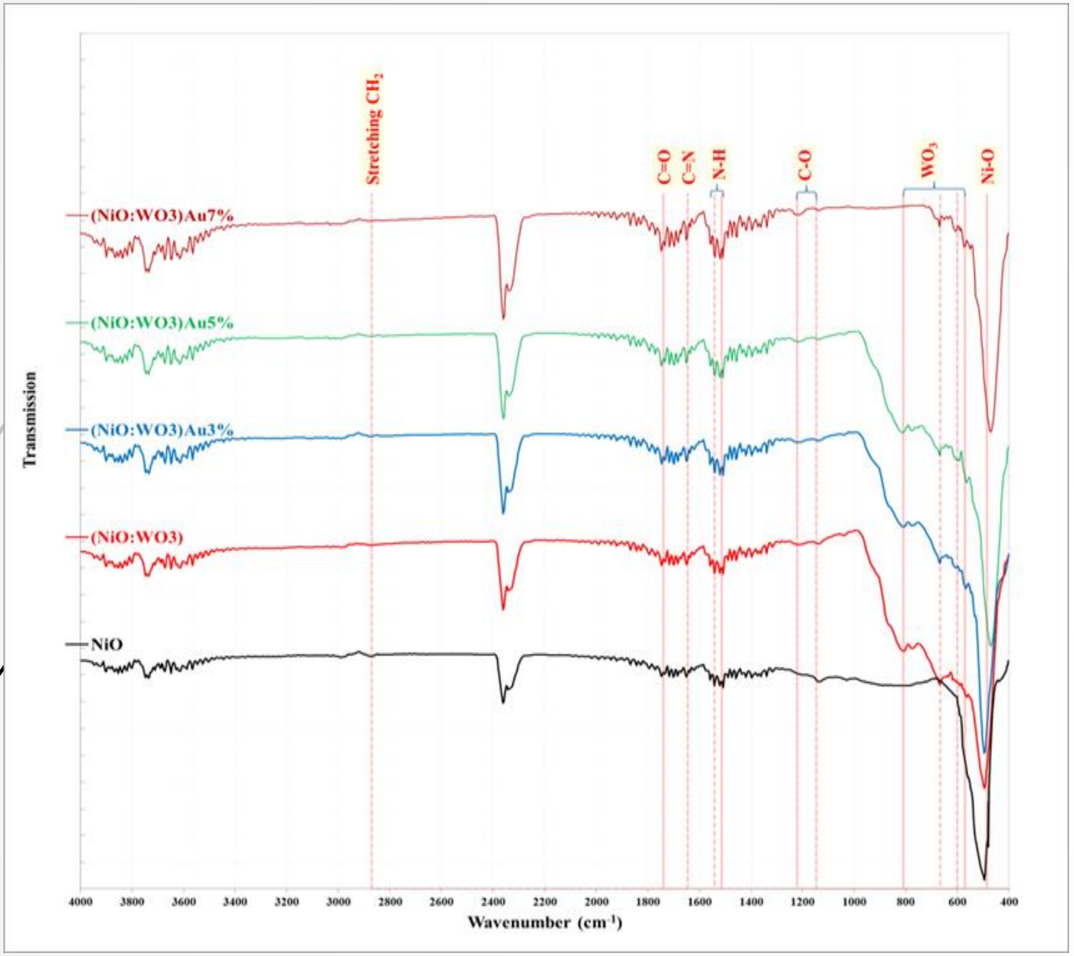


Figure (6): FT-IR spectra of $(NiO:WO_3)1\text{-}x\ Au_x$ thin films at different concentrations of Au prepared at RT

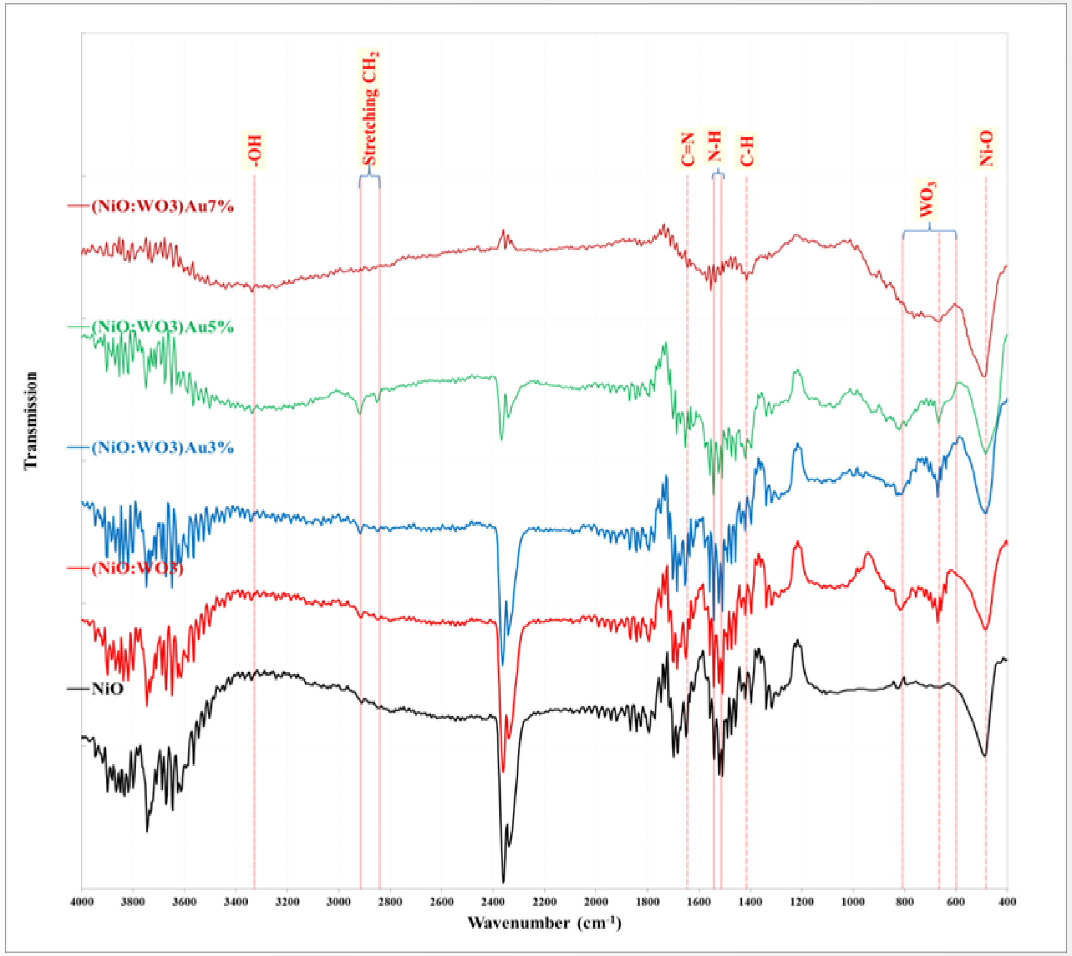
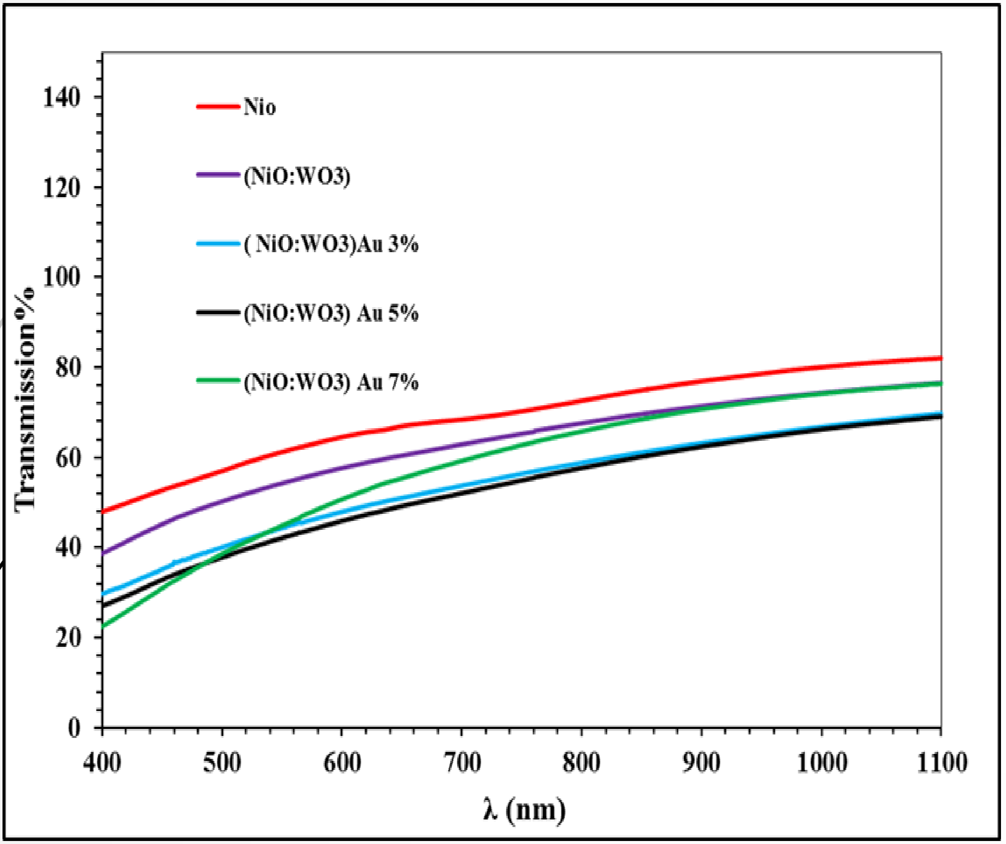


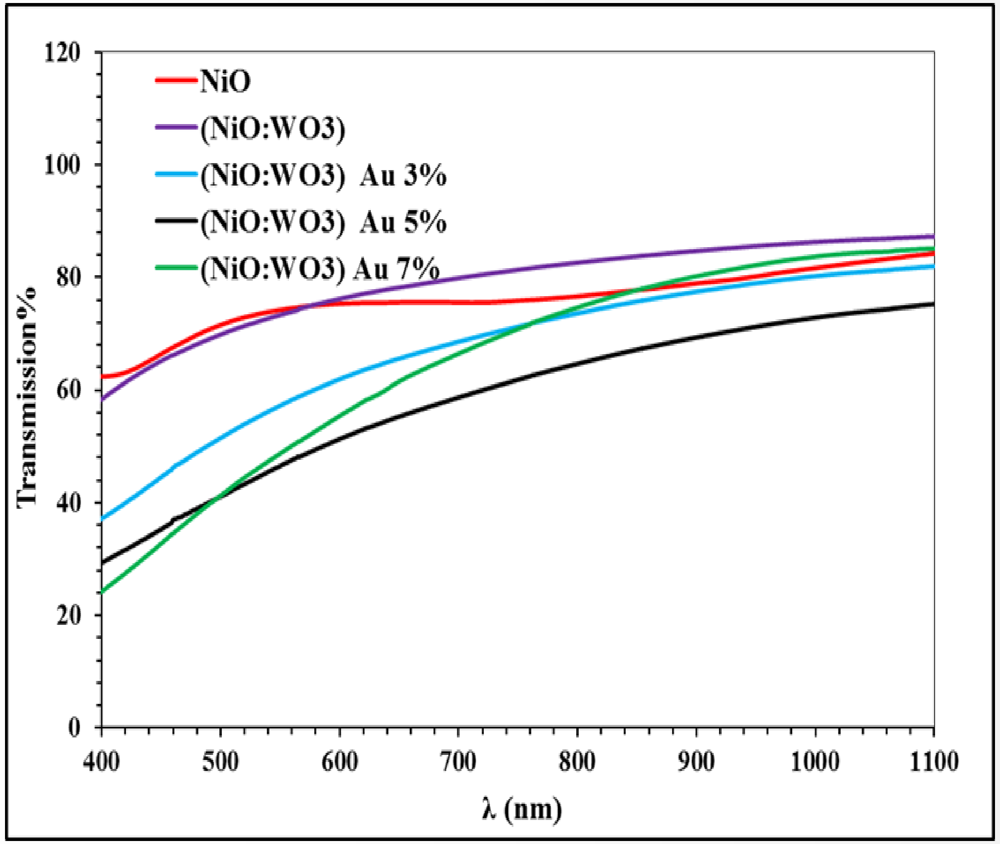
Figure (7): FT-IR spectra of $(NiO:WO_3)_{1-x}\ Au_x$ thin films at different concentrations of Au and annealed to 573K.

The Optical Properties of $(NiO:WO_3)_{1-x}Au_x$ Thin Films

The transmittance



Figure(8):The transmittance as a function of the wavelength for undoped and doped $(NiO:WO_3)_{1-X}$ films with different concentrations of Au_x prepared at room temperature.



Figure(9):The transmittance as a function of the wavelength for undoped and doped $(NiO:WO_3)_{1-X}$ films with different concentrations of Au_x and annealed to temperature 573K.

The absorption coefficient

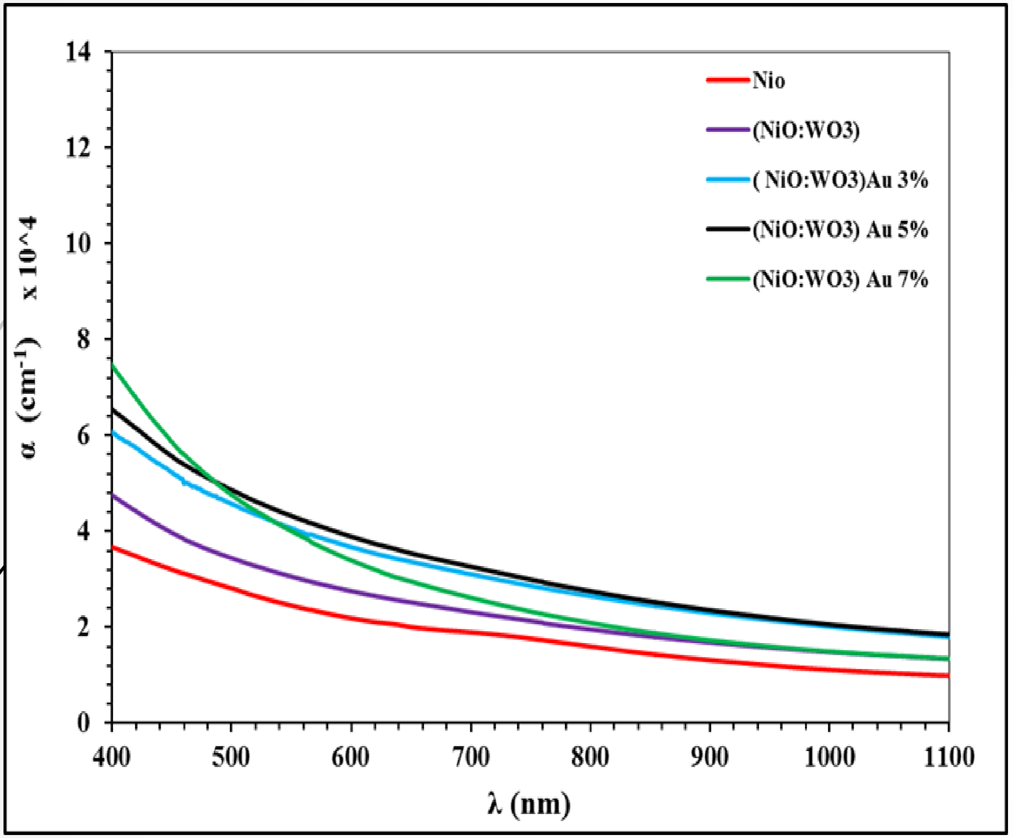


Figure (10): The variation of absorption coefficient with the wavelength for undoped and doped $(NiO:WO_3)_{1-X}$ Au thin films with different concentrations of Au prepared at RT

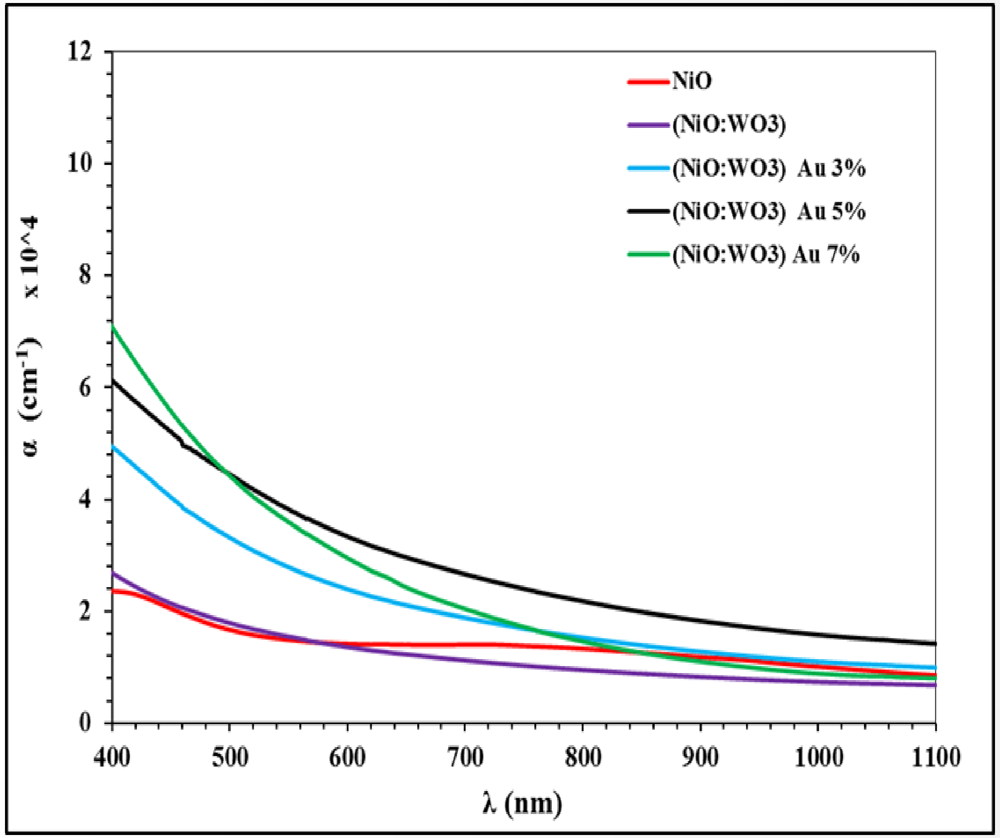


Figure (11):The variation of absorption coefficient with the wavelength for undoped and doped $(NiO:WO3)_{1-X}$ Au_x thin films with different concentrations of Au annealed to temperature 573K.

The optical energy gap

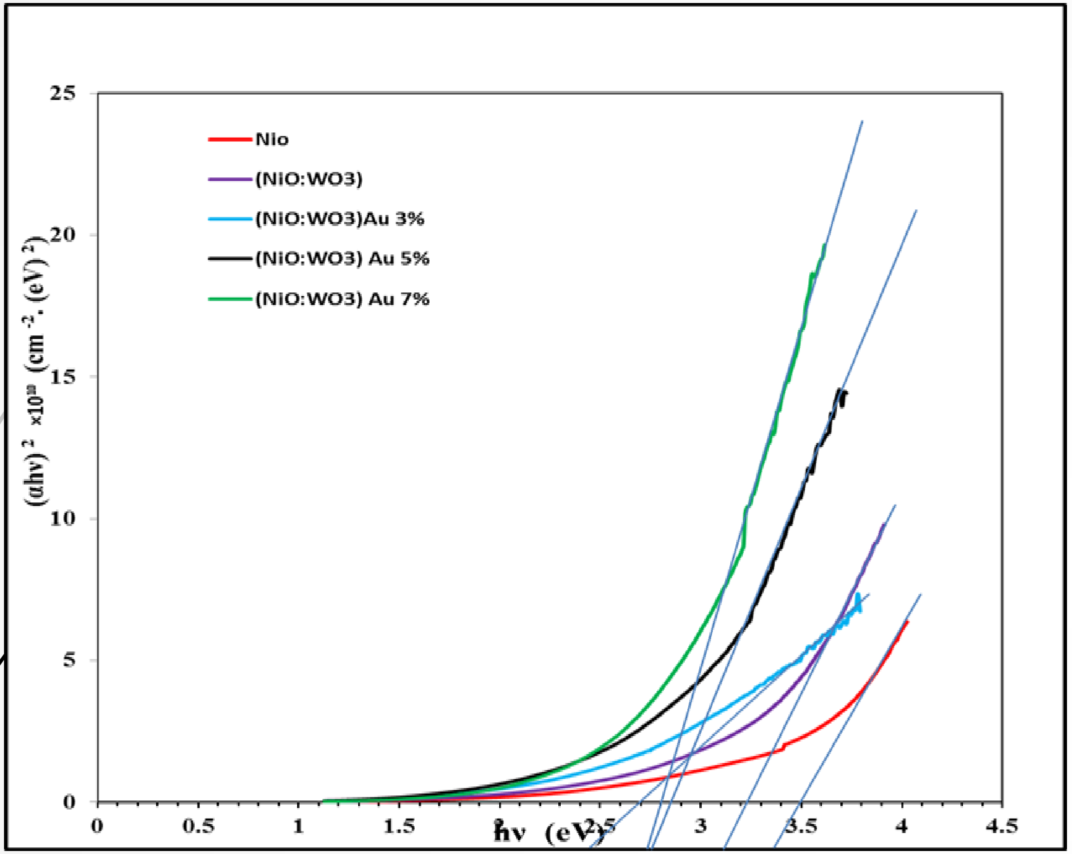


Figure (12):The Variation of $(\alpha h\upsilon)^2$with (hυ) for undoped and doped $(NiO:WO3)_{1-X}Au_x$ thin films with different concentrations of Au prepared at RT.

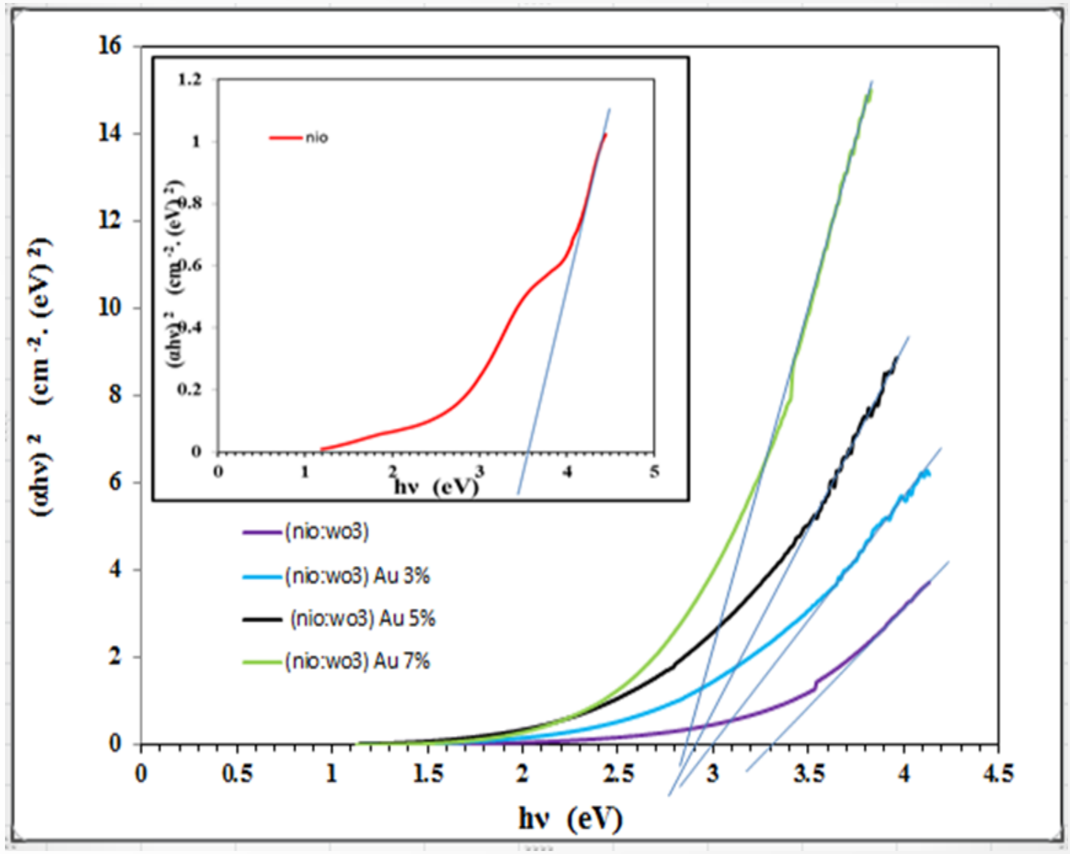


Figure (13):The Variation of $(\alpha h\upsilon)^2$ with (hυ) for undoped and doped $(NiO:WO_3)_{1-X}Au_x$ thin films with different concentrations of Au and annealed to temperature 573K.

The optical constants

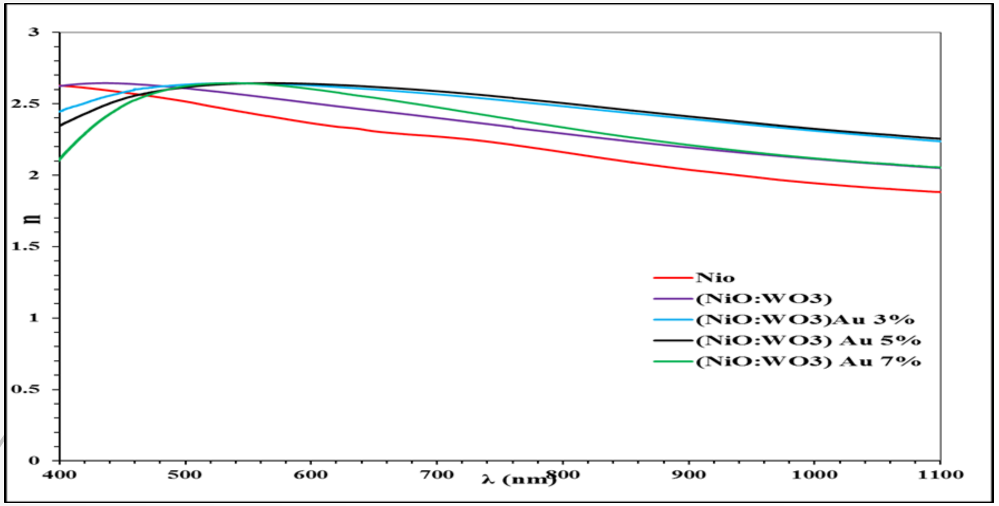


Figure (14):The variation of the refractive index (n) with wavelength for undoped and doped $(NiO{:}WO_3)_{1-X}Au_x$ thin films with different concentrations of Au at RT.

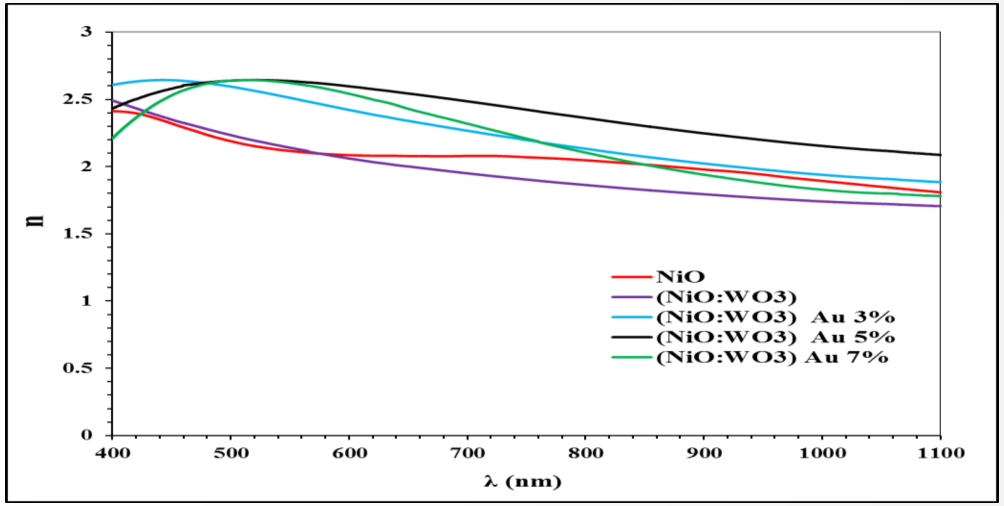


Figure (15):The variation of the refractive index (n) with wavelength for undoped and doped $(NiO{:}WO_3)_{1-X}Au_x$ thin films with different concentrations of Au annealed to temperature 573K

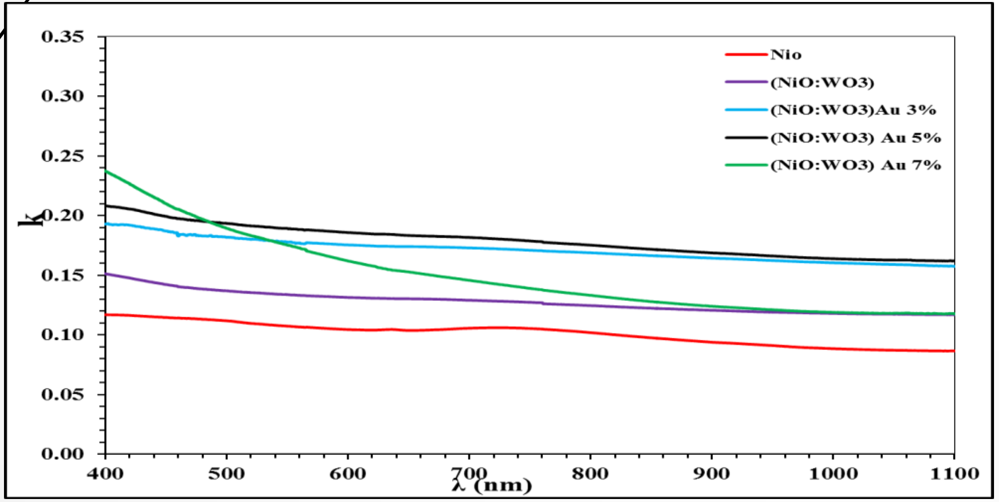


Figure (16):The variation of the extinction coefficient (K) with wavelength for undoped and doped $(NiO{:}WO_3)_{1-X}Au_x$ thin films with different concentrations of Au at RT.

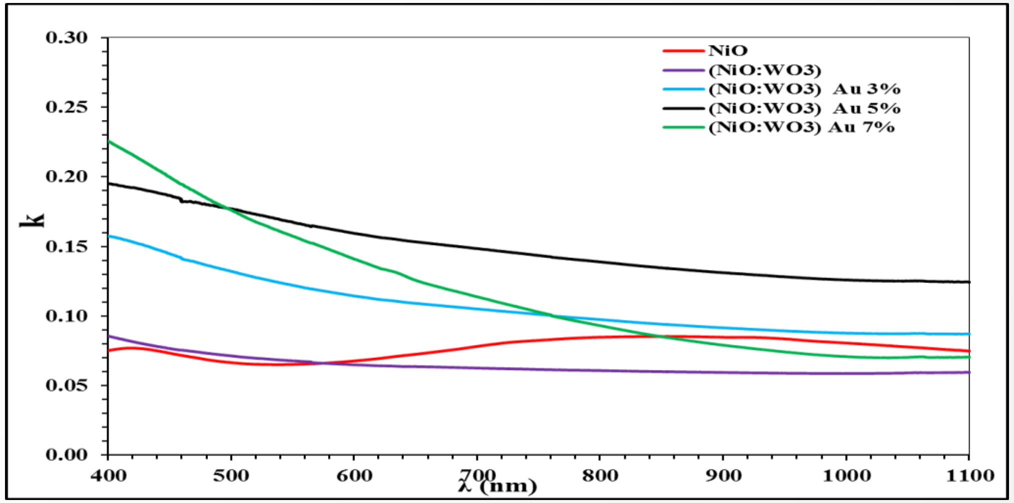


Figure (17):The variation of the extinction coefficient (K) with wavelength for undoped and doped $(NiO{:}WO_3)_{1-X}Au_x$ thin films with different concentrations of Au and annealed to temperature 573K.

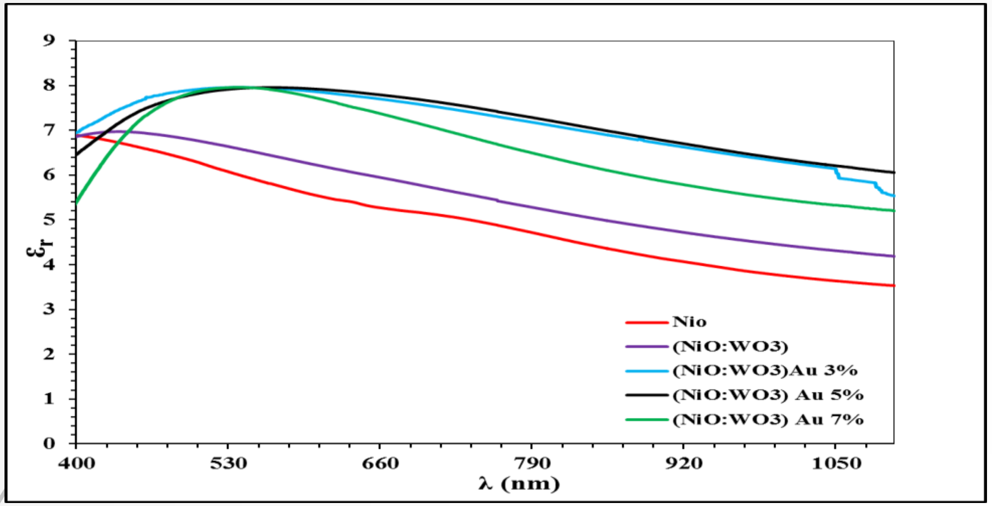


Figure (18): The variation of ε_r with the wavelength for undoped and doped (NiO: WO_3)1-XAux thin films with different concentrations of Au at room temperature.

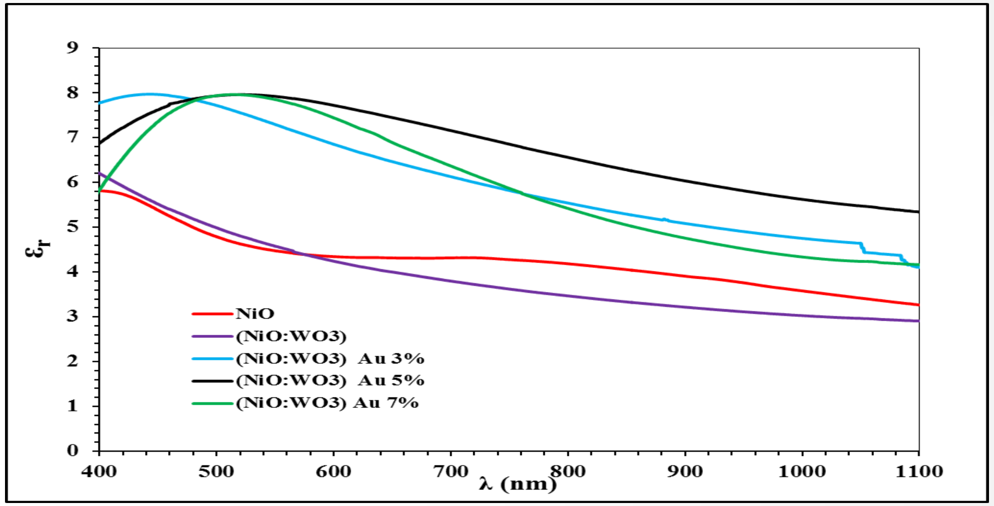


Figure (19) The variation of ε_r with the wavelength for undoped and doped (NiO:WO_3)1-XAux thin films with different concentrations of Au annealed to 573K.

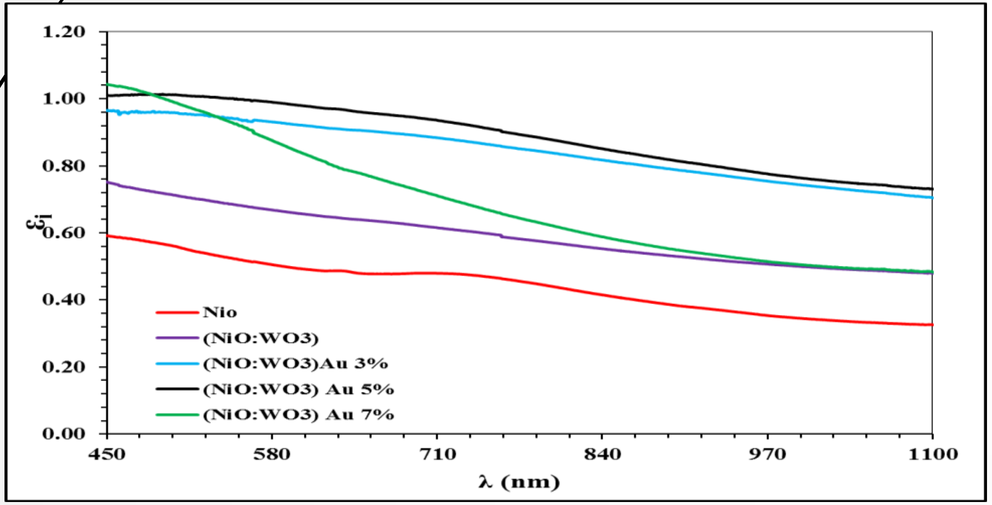


Figure (20):The variation of ε_i with the wavelength for the films $(NiO:WO_3)_{1-X}$ and doped with different percentages of gold Au_x at room temperature.

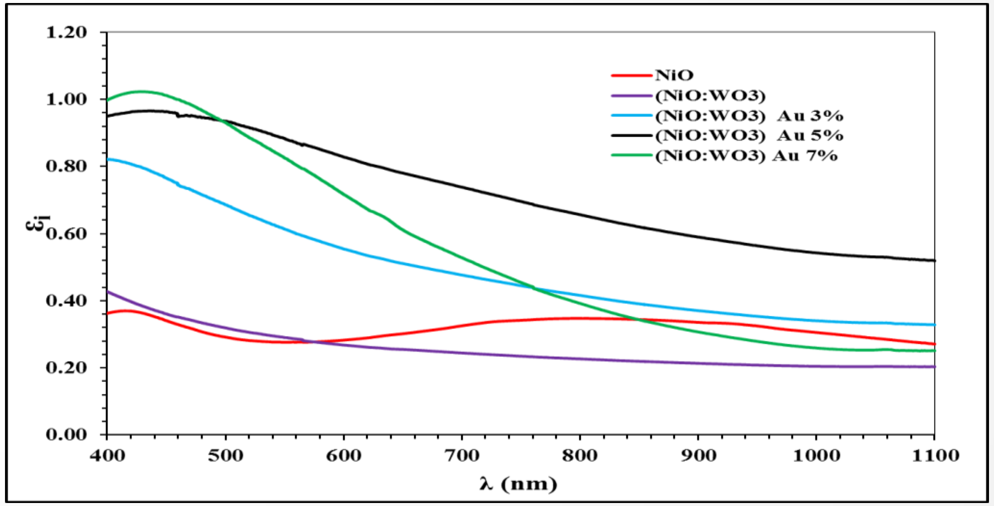


Figure (21) The variation of ε_i with the wavelength for undoped and doped (NiO:WO_3)1-XAux thin films with different concentrations of Au and annealed to temperature 573K.

Table (2): The transmission, Absorption coefficient, and optical constant at RT and annealing temperatures (573 K) for different concentrations of Au for $(NiO:WO3)_{1-X}$ thin films at λ= 450 nm

Sample	T%	α (cm^{-1})	K	n	ε_r	ε_i	Eg (eV)
NiO	52.727	32001	0.114	2.580	6.644	0.591	3.50
$(NiO_{0.85}:WO_{3\ 0.15})$	45.191	39713	0.142	2.641	6.957	0.751	3.25
$(NiO_{0.85}:WO_{3\ 0.15})_{0.97}\ Au_{\ 0.03}$	35.206	52197	0.187	2.578	7.616	0.9646	2.70
$(NiO_{0.85}:WO_{3\ 0.15})_{0.97}\ Au_{\ 0.05}$	32.843	55670	0.199	2.531	7.369	1.009	2.85
$(NiO_{0.85}:\ WO_{3\ 0.15})_{0.97}\ Au_{\ 0.07}$	30.954	58633	0.210	2.482	7.120	1.043	2.80
T=273K.							
Sample	T%	α (cm^{-1})	K	n	ε_r	ε_i	Eg (eV)
NiO	66.382	20487	0.073	2.321	5.382	0.340	3.55
$(NiO_{0.85}:WO_{3\ 0.15})$	65.157	21417	0.076	2.350	5.517	0.360	2.3
$(NiO_{0.85}:WO_{3\ 0.15})_{0.97}\ Au_{\ 0.03}$	44.552	40424	0.144	2.643	7.964	0.765	3
$(NiO_{0.85}:WO_{3\ 0.15})_{0.97}\ Au_{\ 0.05}$	35.246	52139	0.186	2.579	7.619	0.963	2.9
$(NiO_{0.85}:\ WO_{3\ 0.15})_{0.97}\ Au_{\ 0.07}$	32.732	55840	0.200	2.529	7.356	1.011	2.85

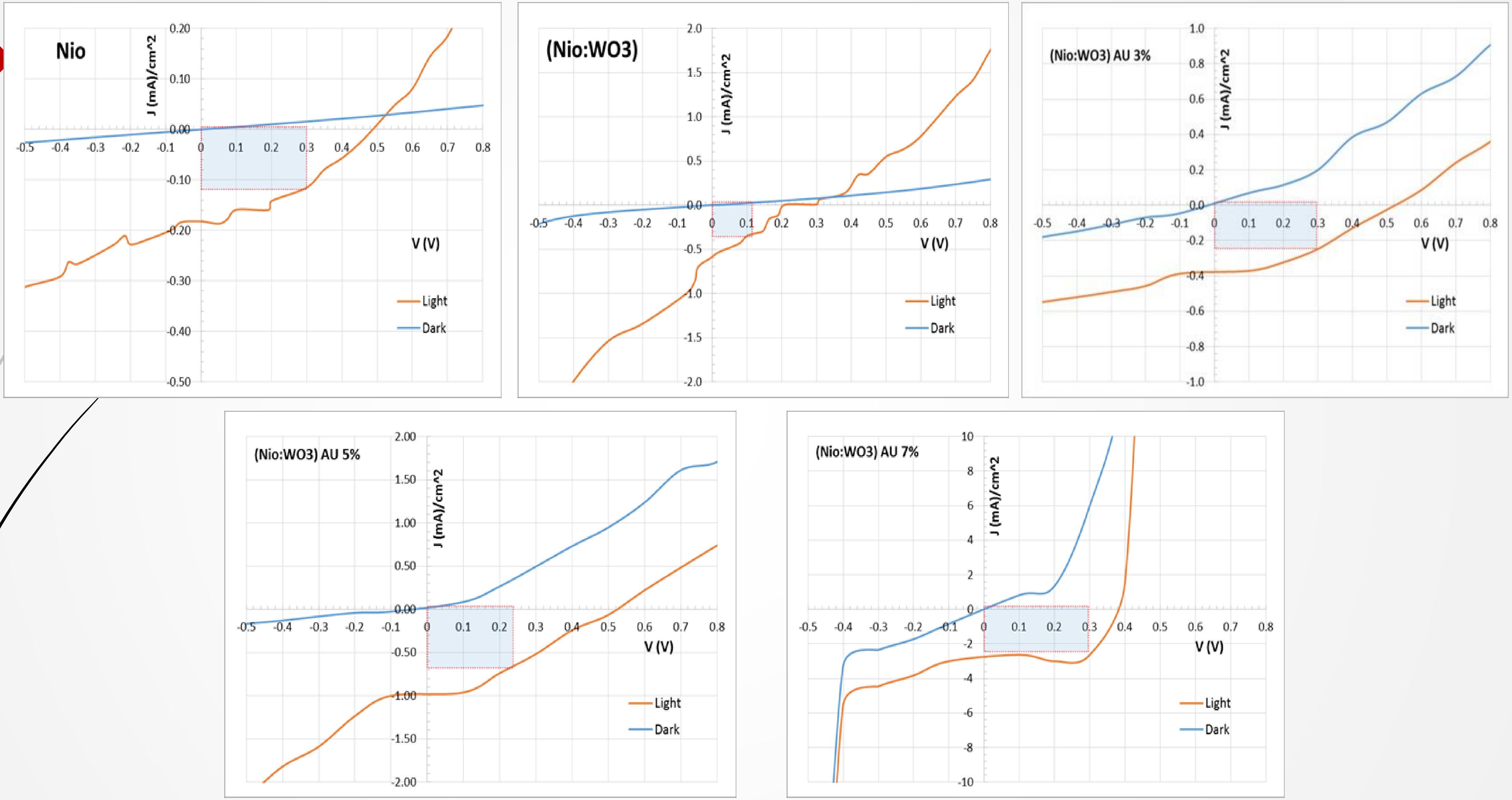
The Electrical Properties of Thin Films

Hall effect measurements

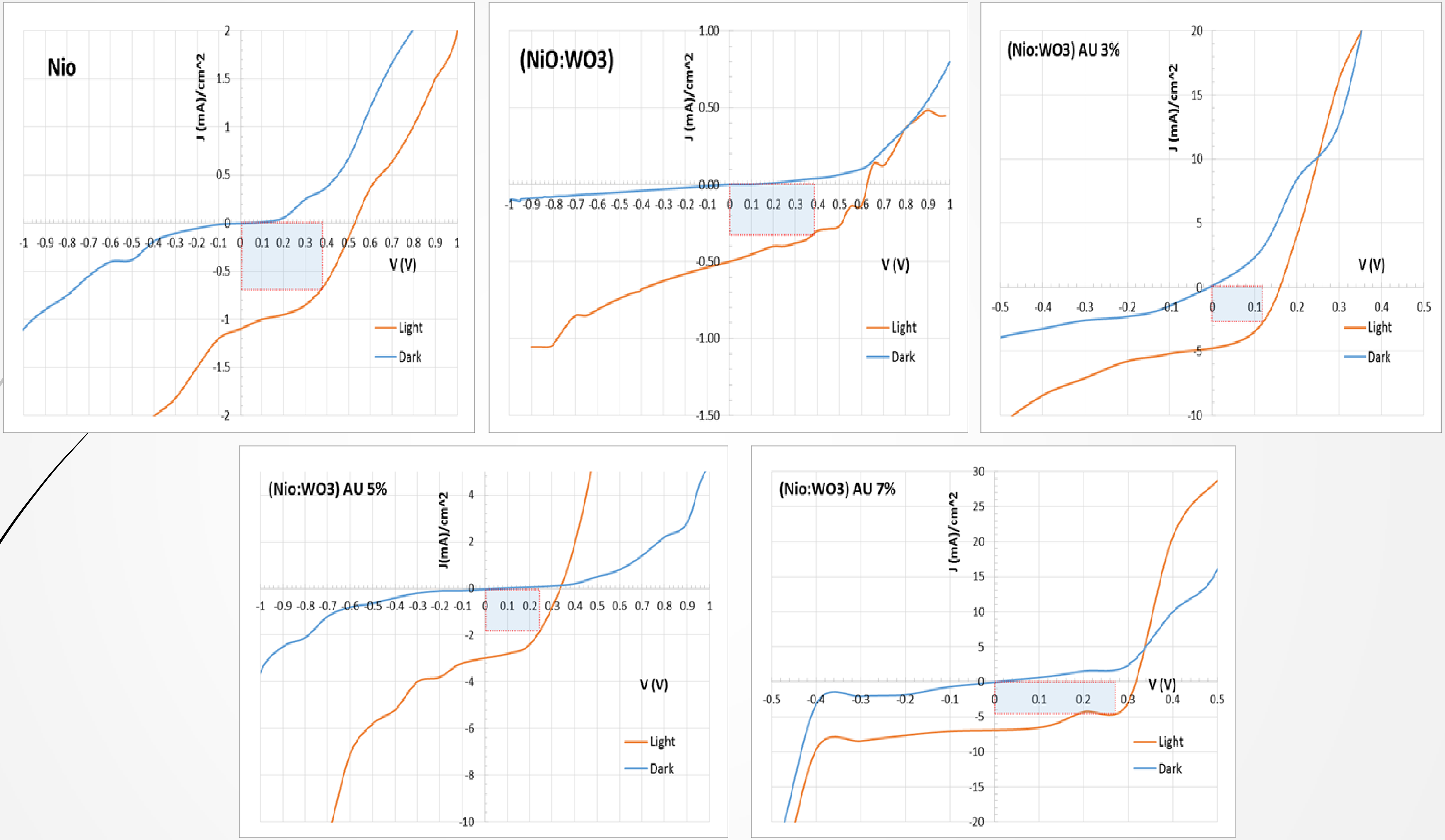
Table (3): The value of the electrical resistivity, Hall coefficient, Hall mobility, carrier concentration and type of conductivity for ($NiO:WO_3$) films doped with different Au at RT and annealed to 573 K .

Sample	σ (1/ Ω Cm)	ρ(Ω cm)	R_H(cm³/c)	n_H(1/cm³)	μ(cm²/v)	type
NiO	2.482E-5	4.029E+4	9.180E+6	6.836E +11	2.267E+2	p-type
($NiO_{0.85}$:$WO_{3\ 0.15}$)	2.411E-5	4.148E+4	3.288+6	1.899E+12	7.926E+1	p-type
($NiO_{0.85}$:$WO_{3\ 0.15}$)$_{0.97}$ Au $_{0.03}$	4.582E-5	2.183E+4	1.104+6	5.654E+12	5.059E+1	p-type
($NiO_{0.85}$:$WO_{3\ 0.15}$)$_{0.97}$ Au $_{0.05}$	3.007E-5	3.325E+4	3.014+6	2.071E+12	9.063E+1	p-type
($NiO_{0.85}$: $WO_{3\ 0.15}$)$_{0.97}$ Au $_{0.07}$	2.655E-5	3.767E+4	1.445E+6	4.318E+12	3.837E+1	p-type
Ta=573K						
Sample	σ (1/ Ω Cm)	ρ(Ω cm)	R_H(cm³/c)	n_H (1/cm³)	μ(cm²/v)	type
NiO	1.207E-4	8.282E+3	5.524E+6	1.130E+12	6.670E+2	p-type
($NiO_{0.85}$:$WO_{3\ 0.15}$)	3.836E-5	2.607E+4	1.528E+6	4.086E+12	5.860E+1	p-type
($NiO_{0.85}$:$WO_{3\ 0.15}$)$_{0.97}$ Au $_{0.03}$	4.995E-5	2.002E+4	3.330E+6	1.875E+12	1.663 E+2	p-type
($NiO_{0.85}$:$WO_{3\ 0.15}$)$_{0.97}$ Au $_{0.05}$	2.613E-5	3.827E+4	-4.021E+6	-1.553 E+12	1.050 E+2	n-type
($NiO_{0.85}$: $WO_{3\ 0.15}$)$_{0.97}$ Au $_{0.07}$	2.212E-5	4.520E+4	5.362E+6	1.164E+12	1.186E+2	p-type

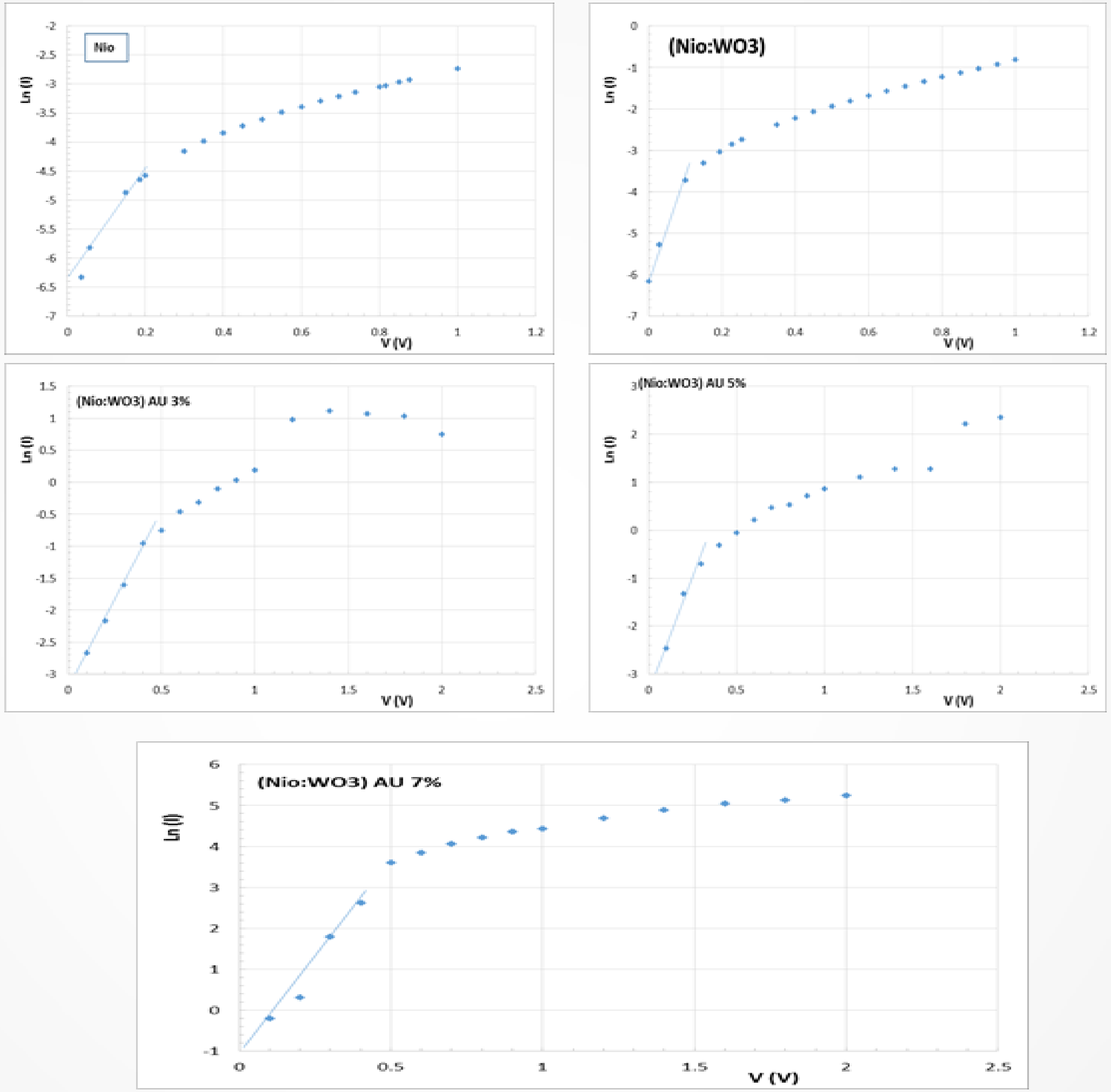
Current-Voltage Characteristics Measurements at Dark and Illumination



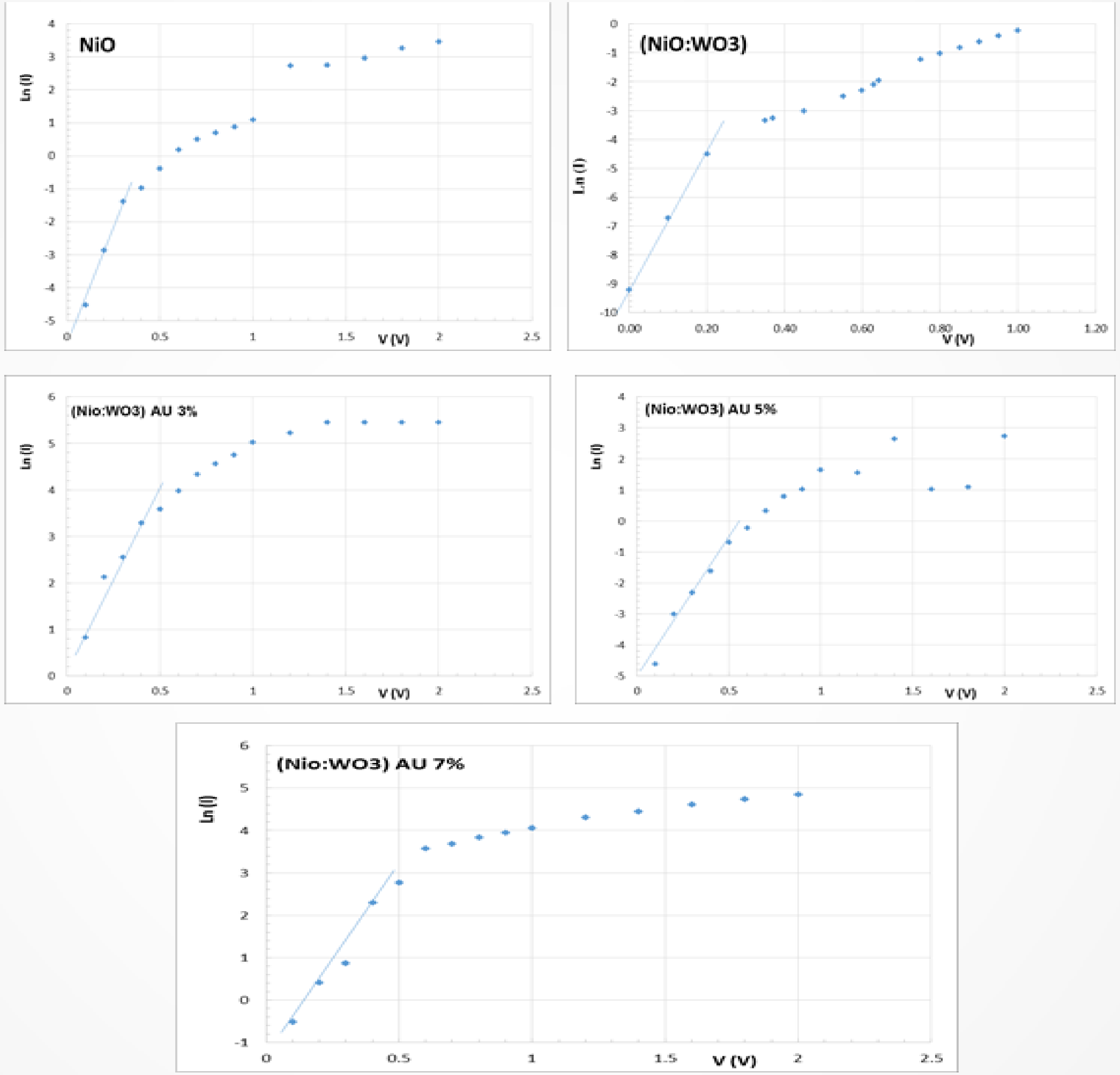
Figures(22) I-V characteristics under dark and illumination by 100mW/cm2 white light for $(NiO:WO3)_{1-x}$ Au_x /p and n-Si with different Au at R.T.



Figures(23) I-V characteristics under dark and illumination by 100mW/cm2 white light for $(NiO:WO3)_{1-x}$ Au_x /p and n-Si with different Au at Ra 573K.



Figures(24) Variation of Ln(I) versus the forward bias voltage for $(NiO:WO3)_{1-x}$ Au_x /p and n-Si with different Au content at RT.



Figures(25) Variation of Ln(I) versus the forward bias voltage for $(NiO{:}WO3)_{1-x}$ Au_x /p and n-Si with different Au content at 573K.

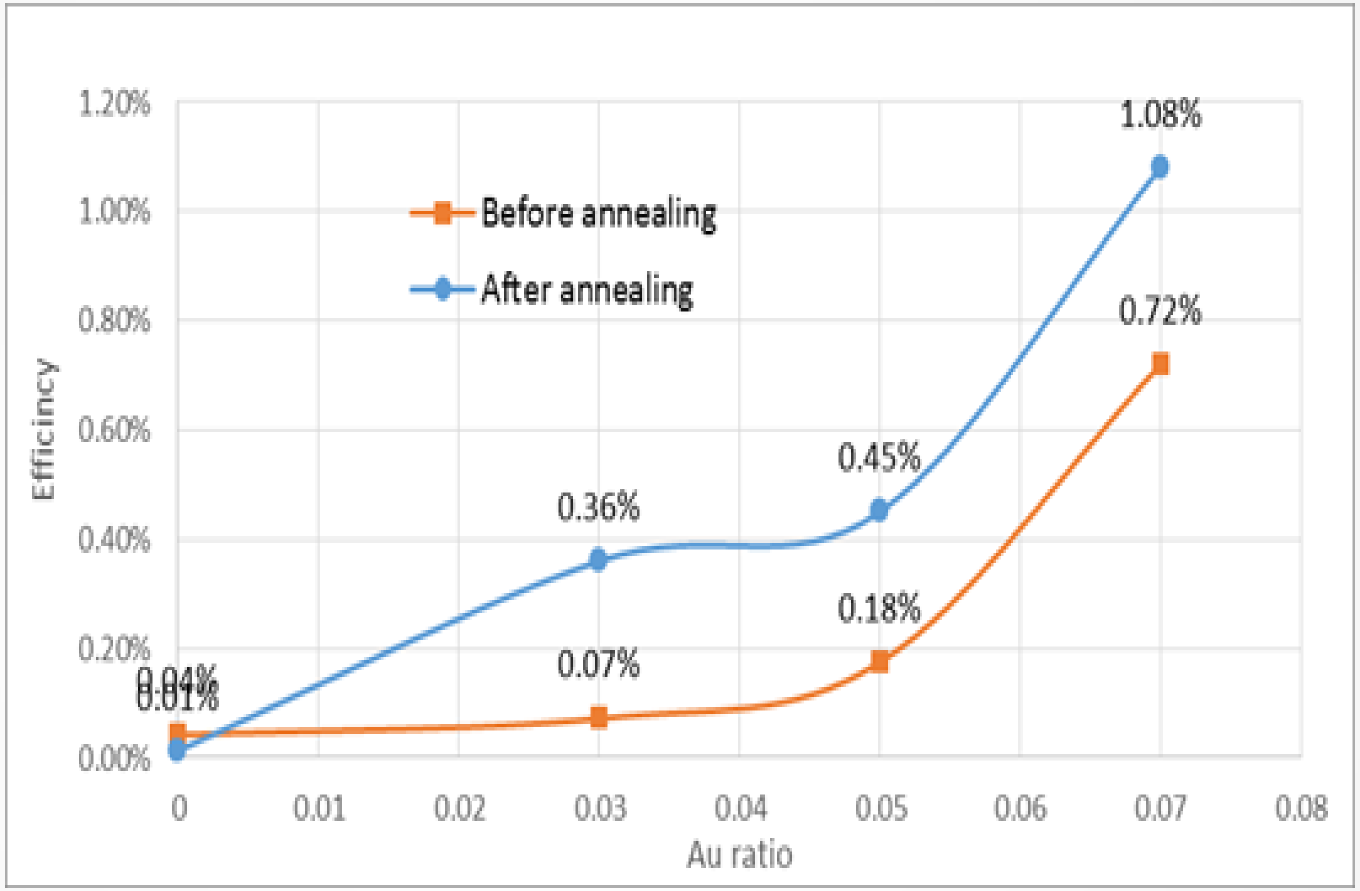


Figure (26) shows the efficiency values for $(NiO:WO3)_{1-x}$ Au_x /p and n-Si with different Au content before and after annealing at a temperature of 573 K .

Table (4) Photovoltaic characterization (V_{oc}, I_{sc}, V_m, and I_m) of $(NiO:WO3)_{1-x}Au_x$ / Si heterojunctions illuminated by 100mW/cm^2 white light with different Au content prepared at RT and annealed to 573 k.

Sample	I_{sc} (mA)	I_m	V_{oc}	V_m	FF	P_m (mW)	Efficincy	idility factor
Nio	0.18	0.12	0.5	0.3	0.400	0.036	0.04%	1.49
$(Nio_{0.85}:Wo3_{0.15})$	0.60	0.35	0.20	0.12	0.35	0.04	0.04%	2.46
$(Nio_{0.85}:Wo3_{0.15})_{0.97}$ Au $_{0.03}$	0.39	0.24	0.52	0.30	0.36	0.07	0.07%	7.01
$(Nio_{0.85}:Wo3_{0.15})_{0.97}$ Au $_{0.05}$	1.00	0.70	0.52	0.25	0.34	0.18	0.18%	4.56
$(Nio_{0.85}:Wo3_{0.15})_{0.97}$ Au $_{0.07}$	2.80	2.40	0.38	0.30	0.68	0.72	0.72%	4.02
Ta= 573 K								
Sample	I_{sc} (mA)	I_m	V_{oc}	V_m	FF	P_m (mW)	Efficiency	ideality factor
Nio	1.20	0.700	0.520	0.390	0.438	0.273	0.27%	2.56
$(Nio_{0.85}:Wo3_{0.15})$	0.05	0.034	0.600	0.400	0.453	0.014	0.01%	1.70
$(Nio_{0.85}:Wo3_{0.15})_{0.97}$ Au $_{0.03}$	5.00	3.000	0.160	0.120	0.450	0.360	0.36%	5.15
$(Nio_{0.85}:Wo3_{0.15})_{0.97}$ Au $_{0.05}$	3.00	1.800	0.340	0.250	0.441	0.450	0.45%	4.74
$(Nio_{0.85}:Wo3_{0.15})_{0.97}$ Au $_{0.07}$	7.00	4.000	0.320	0.270	0.482	1.080	1.08%	4.73

Conclusions

- The ($NiO_{0.85}$:$WO3_{0.15}$) Thin Films doped with different content of Au based0 on PLD Technique have been prepared.

- The XRD results show that the films It a random structure with very small peaks at room temperature. As for annealing at temperature (573 K) it is notice the appearance of three new weak peaks at the level (011), (200) and (02-1), and The quality of the films improved with the increase of the annealing temperature.

- The topography of prepared films show that the results of AFM the roughness decreases in RT and annealed to 573K.
- From XRD and AFM results concluded that the ratio of (0.03) Au is the best between the other ratios
- The Transmittance spectrum decreases with the increasing of Au content in (NiO:WO3) films.
- The energy gap decreases with increasing of Au content at (RT), On the other hand, the annealing process led to an increased of Eg of the films.

- Hall Effect measurement showed that films have either p-type in RT and p-type to all samples except (0.05) when annealing in 573K.
- J-V characteristic showed the maximum efficiency which was 0.72% at RT. After annealing to (573K), it was found that the improvement in the efficiency is increased and led to 1.08%.

Future Work

1. Study the sensing properties for ($NiO:WO_3$) films at the same parameters.
2. Study the Effect of high annealing temperature on the structural, optical and electrical properties of ($NiO:WO_3$) Au.
3. Study the Effect of high annealing temperature on the structural, optical and electrical properties of ($NiO:WO_3$) prepared by sol gel method and doping them by noble metals .
4. Study The A.C conductivity and dielectric constants parameters for our prepared samples under the same conditions.


Thank you!