ISSN NO. 2320-5407

Journal homepage:http://www.journalijar.com ***INTERNATIONAL JOURNAL OF ADVANCED RESEARCH***

RESEARCH ARTICLE

Characterization of (Ni-Mn-Ca-Ag) oxide semiconductors prepared by solid state process

Mostafa M.H. Khalil[1,*] and Osama A. Desouky[2]

1 Chemistry Department, Faculty of Science, Ain Shams University, 11566, Abbassia, Cairo, Egypt

2 Bilbis Higher Institute of Engineering (BHIE), Bilbis, Sharqia, Egypt

Manuscript Info

Manuscript History:

Received: 15 July 2014

Final Accepted: 26 August 2014

Published Online: September 2014

Key words:

Corresponding Author

Mostafa M.H. Khalil

Abstract

NiO -MnO_2 semiconductors have been synthesized by a solid –state method. The prepared semiconductors have been characterized using X-Ray Diffraction, DTA, thermo gram and SEM. The (SEM) of the Mn- doped NiO samples have certain type of grain and also the voids take place between the grains. It is also found that the Mn, Ca, and Ag atoms are diffused into the NiO grains. In addition to $NiMnO_3$ and Ni_3Mn grains are observed. The thermo gram show two endothermic effect. Mixes representing NiO , CaO, MnO_2 and Ag_2O additives show very good plateau in (I-V) relation . The non-lineare behavior in NiO base materials is attributed to the formation of interface states in the band gap of NiO which lead to the development of potential barriers to electrical conduction at NiO grain boundaries. The decrease of capacitance in (pf) , dielectric constant (ε^-) and consequently increase (AC) conductivity with increasing frequency (1 – 20) KHz . A decrease in resistance and resistivity with rise in frequencies indicates a possibility of increase in the AC conductivity with increase frequency.

1. Introduction

Semiconductor nanocrystals are the subject of a thriving area of physical and synthetic inorganic chemistry, motivated by both fundamental science and the long-term technological potential of these materials. Semiconductor nanocrystals are already commercially marketed for application as luminescent biolabels (Chan and Nie, 1998, Gao and Nie, 2003, Bruchez et al, 1998). and have been demonstrated as components in regenerative solar cells (Zaban, et al 1998 , Huynh et al 2002) , optical gain devices Klimov et al 2000) , and electroluminescent devices (Colvin et al 1994, Dabbousi et al 1995 , Coe et al 2002). A potentially far greater market awaits these materials in the area of information processing technologies if the numerous and daunting challenges associated with nanoscale technology can eventually be overcome. Nickel(II) oxide is a notable and well studied material among various transition metal oxides because of its unique advantage in terms of properties and applications, such as p-type transparent conducting film (Sato et al 1993), electro chromic devices (Kitao et al 1994) gas sensors (Hotovy et al 2002), spin-valve devices (Neel temperature being 523 K) (Kumagai et al 1996), cathode in alkaline batteries, etc. Nickel oxide (NiO) is the most exhaustively investigated transition metal oxide. It is a NaCl-type anti ferromagnetic oxide semiconductor. It offers promising candidature for many applications such as solar thermal absorber , catalyst for O_2 evolution (Cook and Koffy 1984), photo electrolysis (Botejue and Tseung 1985) and electro chromic device (Benko 1981). Nickel oxide is also a well-studied material as the positive electrode in batteries (Lampert 1984). Pure stoichiometric NiO crystals are perfect insulators (Vincent 1987). Several efforts have been made to explain the insulating behavior of NiO. Appreciable conductivity can be achieved in NiO by creating Ni vacancies or substituting Li for Ni at Ni sites (Bosman and Crevecoeur 1966). Most attracting features of NiO are: (1) excellent durability and electrochemical stability, (2) low material cost, (3) promising ion storage material in terms of cyclic stability, (4) large span optical density, and (5) possibility of manufacturing by variety of techniques. Nickel oxide thin films have been prepared by various techniques that involve: vacuum evaporation (Tsu et al 1969), electron beam evaporation (Seike and Nagai 1991), magnetron sputtering (Sato et al 1993, Hotovy et al 1998), anodic oxidation (Lampert et al 1986), chemical deposition (Pramanik and Bhattachraya 1990, Varkey and Fort 1993; Chigane and Ishikawa 1998), atomic layer epitaxy (Utriainen et al 1998), sol–gel (Surca et al 1996) and spray pyrolysis technique (SPT) (Xie et al 1996, Misho et al 1988, Kadam et al 1997) . WurtziteNiO (*w*-NiO) has been found to display half-metallicity (Wu et al 2006) . Also *w*-NiO was found to have a small lattice mismatch with those most popular wurtzite wide gap semiconductors such as ZnO, GaN, and SiC. So even though wurtzite structure is a metastable phase for NiO, its stability may be achieved by epitaxially growth on those semiconductor substrates. Then if half-metallicity of *w*-NiO is not destroyed at the interface, injection of 100% spin polarized electrons will be achieved. Among those wide gap semiconductors ZnO is the most promising candidate of substrate material ,since the common O element of both ZnO and NiO enhances the possibility of successful epitaxial growth of this kind. Also the interface O atomic monolayer makes Zn and Ni atoms separated and their interaction screened to some degree. So this interface configuration may have a relatively small effect on the electronic properties and thus *w*-NiO will keep half-metallicity. For ZnO and its related materials, NiO layer can be a good candidate for NiO–ZnO*p-n* junction hetero structure because oxygen-rich NiO is known as p-type semiconductor with a band gap of 3.54 eV. While NiO has an ant ferromagnetic property, Ni itself is a ferromagnetic material, and hence incorporation of transition metal such as Ni into semiconductors can affect magnetic properties of semiconductor host materials. Therefore, Ni-doped ZnO can be an example of diluted magnetic semiconductor material (He et al 2002). This paper is to investigate the influence of MnO2 additives on microstructure, nonlinear properties, and electrical characteristics of NiO-CaO-Ag_2O semiconductors.

2. Materials and Methods

The following raw materials were used to satisfy the suggested composition, reagent grade (BDH) powders NiO, CaO,Ag_2O, and MnO_2, were used for the study. Three mixes were suggested to study the effect of MnO2 doping on the properties of NiO-CaO- Ag_2O is given in Table 1. The prepared NiO, Ag_2O, CaO and MnO_2 were wet ground in a ball for a period of 3 hour to pass 200 mesh sieves. The slurry was dried over night and used to fulfill the above mentioned mixes. The mixes were weighed in the suggested proportions, wet milled to ensure through mixing of the different compositions then dried at 110 ^oC. Two discs were used, the first one has 1.2 cm diameter and 0.2 cm thickness, and the second disc has 5 cm diameter and 0.2 cm thickness. These two discs were processed by a semi-dry press method under 70 KN. Small specimens were subjected to thermal treatment to select the proper maturing temperature for each mix. Three discs were always fired in muffle kiln with a rate of heating of 5 ^oC/ min in the temperature range between (900 -1200)^oC and for2 hours . The sinterability of the different samples was determined in terms of physical properties.

The XRD of different mixes were examined by using Philips apparatus type 170, a vanadium (λ=1.54 A^o) and Ni-filter in Metallurgy Research Center, Egypt. A continuous plot of intensity for 2θ values 4 to 80 was made at a scanning speed of 1^o/ minute, with a paper speed of 10 mm/min.Both surfaces of the samples were lapped and ground with SiC paper and polished with Al_2O_3powder to a mirror like surface. The polished samples were thermally etched at 1100°C for 30 min. The surface microstructure was examined by a scanning electron microscope (SEM, Joel- JEM. T 200).DTA locates the ranges corresponding to the thermal decomposition of different phases in paste, while TG measures the weight loss due to the decomposition. TG coupled with DTA makes it possible for the hydration reaction to be followed qualitatively, semi-qualitatively and quantitatively. Such thermal analysis is useful to observe the evolution of the hydration and especially to estimate the process of different reaction. Although these techniques are more suitable for studying hydration at later stages, they can be used as here, to consider the early phase of hydration accelerated by high temperature curing. Concerning DTA, 40µm powder specimens were placed in a refractory steel crucible and analyzed using a hybrid system with oven-drying at a heating rate of 5.8^o C/min up to 95 ^{o}C. Sample masses ranged from 1.00 to 1.10g. In the case of TG, the specimen (40 µm powder) were introduced into a quartz crucible and analyzed using system at a heating rate of 7.5^oC/min up to 600^oC. Masses of sample were between 200 and 220mg. No trace of calcium carbonate was detected during analysis as the freeze–drying technique prevented carbonation of the sample hence thermo grams will be presented up to 600 ^oC for DTA and 650^oC for TG . The PM 6304 program able automatic RCL meter was used for precise measurements of resistance, capacitance and inductance. From the measured values of capacitance, the dielectric constant at all frequency from 1 KHz – 200 KHz was calculated at constant temperature**)**, simple equivalent circuit repressing a metal oxide semiconductors as a capacitance in parallel with a voltage dependent resistor as shown in Fig 1 .

.

The capacitance and resistance at constant temperature were measured at different between (1-30) KHz and the respective permittivity [ε⁻] was calculated according to the following relations :

$$\varepsilon^{-} = \frac{C\, d}{\varepsilon_o\ A}$$

Where C = capacitance In farad.
d = thickness of specimen in m.
ε_o= dielectric constant of vacuum 8.85 $\times 10^{-12}$ F/m.
A = area of specimen in m^2.
Also from the values of resistance [R], the resistivity [ρ] and conductivity [σ] were calculated from the following relation:

Resistivity [ρ] = $\frac{R\,A}{d}$ Conductiviy (σ) = $\frac{1}{\rho}$

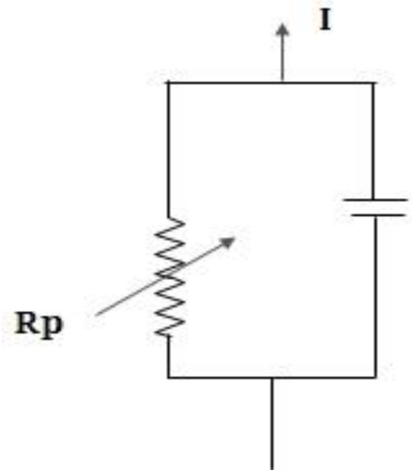


Fig .1.simple equivalent circuit representing a metal oxide semiconductors as a capacitance in parallel with a voltage dependent resistor

Table (1) Composition of different mixes in mol%.

Oxides	**NiO**	**MnO_2**	**CaO**	**Ag_2O**
C1	**98.1**	**0.9**	**0.4**	**0.6**
C2	**98.3**	**0.7**	**0.4**	**0.6**
C3	**98.5**	**0.5**	**0.4**	**0.6**

3. Results and discussion

Results of XRD of different mixes are present in Fig . 2 , shows the X-ray diffraction pattern of [C_1] annealed at 1050 ^oC for 10 min in oxygen atmosphere in which , Nickel oxide – NiO –Hexagonal phase(RH) –(a= 2.9552 b=2.9552 c= 7.2275) at about 2θ= 37. 305 d= 2.40850A^o, 2θ= 43.344 d= 2.08587A^o, 2θ=62.95 d= 1.47531A^o, 2θ= 75.467 d= 1.25868A^o, 2θ= 79.455 d=1.20522A^o[PDF number is (166) -3-54.6629]. The diffraction peak at 2θ=91.269 d= 4.60265A^o , 2θ= 21.442 d= 4.14079A^o, 2θ=27.211 d= 3.27457A^o, 2θ=33.536 d= 2.67008A^o, 2θ=44.766 d=2.02288A^o , 2θ=35.046 d= 2.55839A^o,2θ=40.238 d= 2.23941A^o , 2θ=53.292 d=1.71759 A^o, 2θ=56.075 d=1.63876 A^o, 2θ=67.297 d= 1.39020 A^o, 2θ=67.85 d= 1.38020A^o, 2θ=73.997 d= 1.2800A^o, corresponds to Nickel oxide [PDF number is (227) -16-1073.74].Fig. 2. shows the X-ray diffraction pattern of sample [C_2] annealed at 1050 ^oC for 10 min in oxygen atmosphere in which, Nickel – NiO , Hexagonal phase (RH) a=2.954 b=2.954 c= 7.236 at about 2θ=43.429 d=2.082A^o, 2θ= 37.398 d= 2.40273A^o, 2θ=63.008 d= 1.47410A^o , 2θ=75.521 d= 1.25792 A^o, 2θ=79.486 d= 1.20483A^o,[PDF number is (166)-3-54.6827] . Nickel Manganese oxide – Ni_6MnO_8 – Cubic phase –(a=8.324 b=8.324 c= 8.324

) at about 2θ=37.398 d= 2.40273A^o, 2θ=43.429 d= 2.082A^o, 2θ=63.008 d= 1.47410 A^o [PDF number is 9225)]. The diffraction peak at 2θ=27.267 d= 3.26804A^o,2θ=35.128 d =2.55260A^o corresponds to Manganese oxide , (Tetragonal phase , (a=8.6969 b=8.6969 c=5.981 [PDF number is (135) -4-4] . Fig .2. shows the X-ray diffraction pattern of sample [C_3] annealed at 1050 ^{o}C for 10 min in oxygen atmosphere in which, Nickel oxide - NiO , Hexagonal (RH) a=2.9552 b=2.95520 c = 7.2275 at about 2θ=37.313 d= 2.40799 A^o, 2θ= 43.338 d= 2.08617 A^o, 2θ=62.95 d= 1.47532A^o, 2θ=75.466 d = 1.25869A^o, 2θ=79.448 d =1.20531A^o,[PDF number is (166) – 3 – 54.6629] . The diffraction peak at 2θ= 27.222 d =3.27333A^o , 2θ=35.041 d= 2.5587A^o , 2θ=38.835 d= 2.31704A^o, 2θ=40.226 d= 2.24006A^o, 2θ=44.351 d =2.04081A^o, 2θ= 53.266 d=1.71837A^o,2θ= 56.069 d=1.63894A^o corresponds to Nickel oxide ,Tetragonal phase - a=4.6415 b=4.6415 c= 9.223 , [PDF number is (136) -2-198.696-1] .

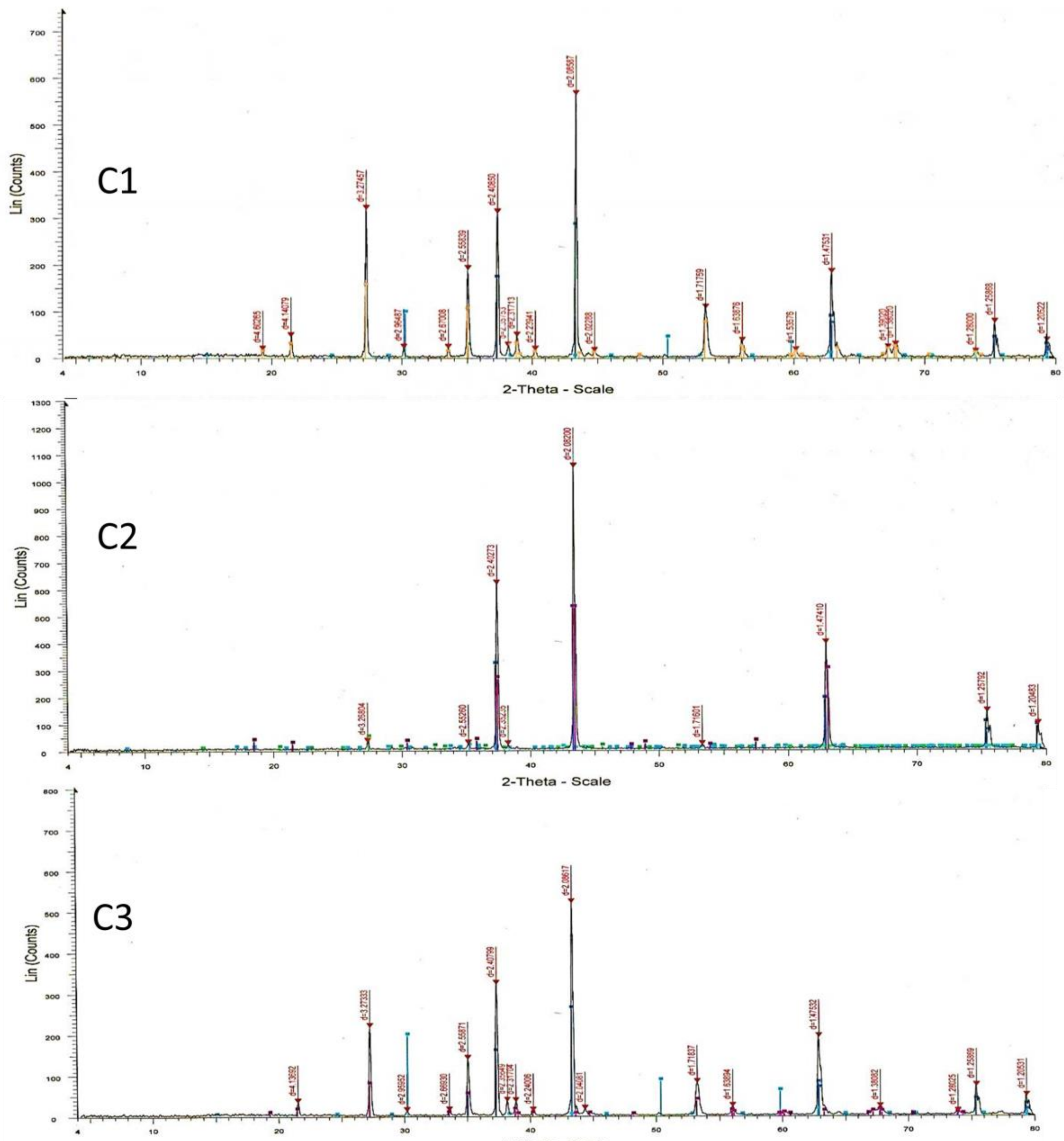


Fig 2. XRD of different mixes [NiO, Ag_2O, CaO, MnO_2]

Fig .3.shows DTA, thermogram of sample [C_1] which containing (1.837) wt %Ag_2O, (0.295) wt% CaO, (1.033) wt % MnO_2 and (96.834) wt% NiO. The thermo gram show two endothermic effect in which, the onset point (63.97) ^oC, the peak 1 top at (82.11) ^oC, the offset at (85.29)^oC, Enthalpy/µV.s/mg is 5.4669, the onset point (234.32) ^oC ,the peak 1top at (241.91) ^oC, the offset at (245.18) ^oC, Enthapy/µV.s/mg is (0.2808) .

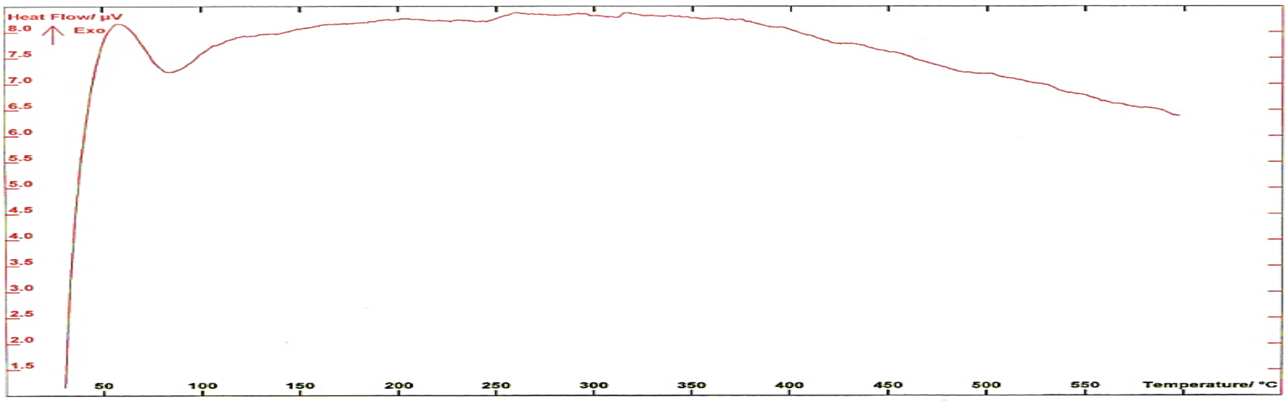
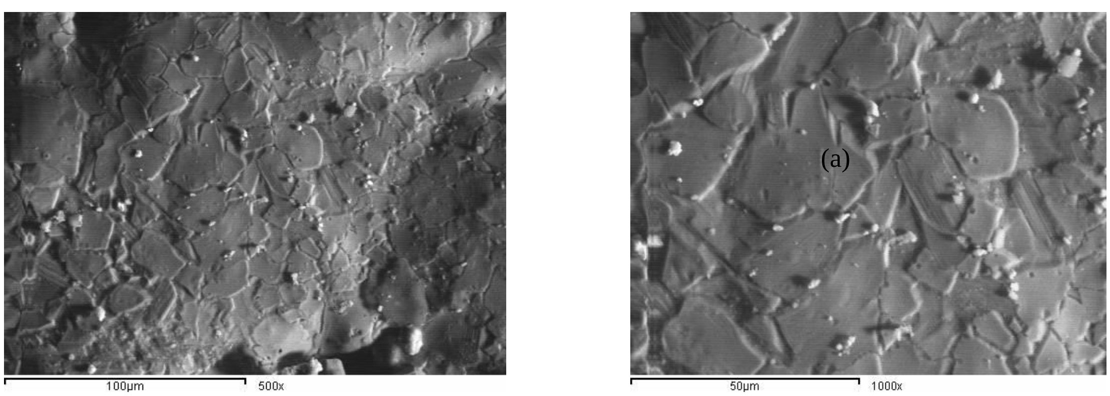


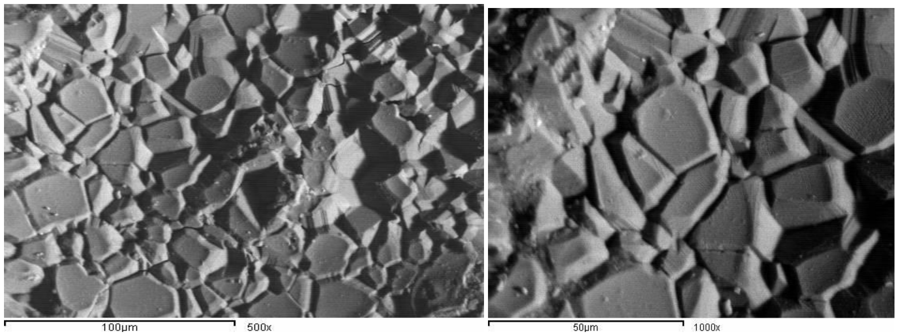
Fig .3 . The DTA of mix C1

The SEM mixes containing NiO, CaOand MnO_2 present in Figs. 4,5 . SEM of mix (C_1), which containing (1.0337) mol % MnO_2 in Fig. 4., shows exsolution two imssibol liquid phase, grain growth, grains pelt shape, melt phase, crystalline phase, exsolution miscibility and Mn enter the lattice of Ni. The microstructure Mn-doped NiO has the certain type grain , the voids take place between the grains. It is found that the Mn, Ca, and Ag atoms are diffused into the NiO grains. The grains in microstructure may have an important effect on electronic properties of the sample.SEM of mix (C_2) which containing (1.4510) mol % MnO_2 and (0.295) mol %CaO, present in Fig. 5.showed, grain growth of NiO grains in preferred orientation Mn enter the lattice of NiO, grain pelt shape and crystalline phase.



(a) (b)

Fig .4.SEM of mix (C_1), a) Thermally etched surface, general view X = 500. b)Thermally etched surface, showed two phases NiO grains and intergranular phase at triple point X = 1000.



(a) (b)

Fig .5. SEM of mix (C_2) Thermally etched surface, general view X = 500. Thermally etched surface growth in preferred orientation in NiO grains, X = 1000.

Mixes containing NiO, CaO, MnO_2 and Ag_2O additives show very good plateau in (I-V) relation as shown in Fig.6. The non-linear behavior in NiO base materials is attributed to the formation of interface states in the band gap of NiO which lead to the development of potential barriers to electrical conduction at NiO grain boundaries.

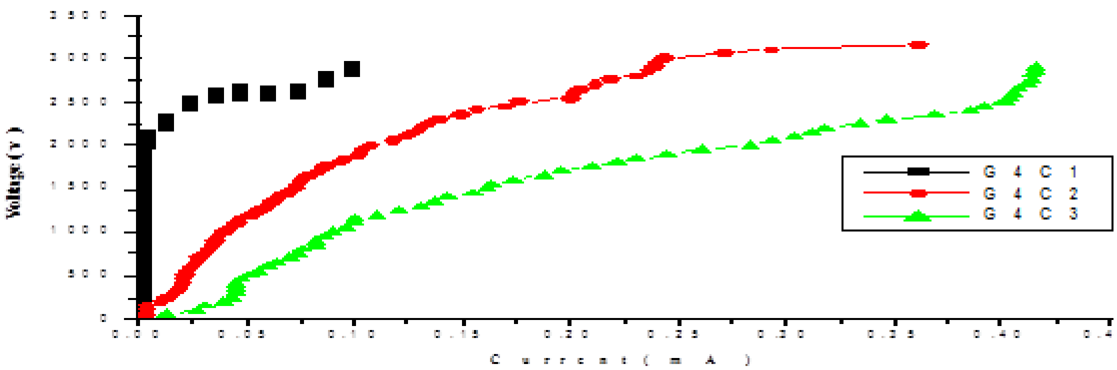


Fig. 6 (I-V) characteristics of different mixes

Fig. 7.shows the variation of dielectric constant ε^- with frequency (1-20) KHz for prepared samples $NiCaMnAgO_4$ of different mixes. It is clearly observed from this Fig that the dielectric constant ε decreases with increase frequency for $NiCaMnAgO_4$ samples, in a behavior similar to that exhibited by most semiconducting materials (Fayek et al 1992). The dielectric constant was increased with decreasing the mol% MnO_2 in present of Ag_2O and CaO. In the presence of Ag_2O, the samples become more conducting .Dielectric constants are maintained at constant values as frequency increases up to 5 KHz. But at 5KHz abrupt change in dielectric constant which is caused dielectric relaxation is shown for all the powder amounts of different mixes. The relation is presumably due to change of polarization mode of $NiCaMnAgO_4$ powders with frequency, transferring from dipole polarization to ionic polarization region.

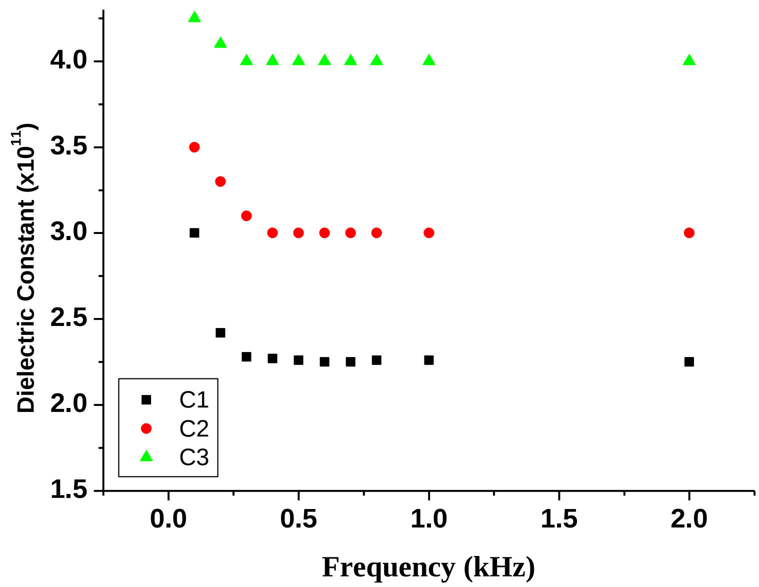


Fig .7. Effect of frequency (KHz) on dielectric constant of different mixes

Fig. 8 .shows Ac conductivity plots of conductivity versus frequency of Mn-Ca –doped NiO . It is apparent from the figure that the conductivity exhibits a semiconductor behavior with frequency. This suggests that the activation energy required for the hopping process in the Mn- Ca-Ag-doped NiO is low. This activation of charge carrier is indicative of a hopping conduction mechanism. The activation energy decreases with increasing frequency . This suggests that the applied field frequency enhances the electronic jumps between the localized states and ,that is why ,activation energy decreases with frequency. X-ray diffraction pattern of mixes annealed at 1050 ^{o}C for 10 min in oxygen atmosphere in which , Nickel oxide , NiO (Hexagonal phase),nickel , nickel manganese oxide , Ni_6MnO_8(Cubic phase) .In general , the decrease of capacitance in (pf) , dielectric constant ($\varepsilon^{'}$) and consequently increase (AC) conductivity with increasing frequency (1 – 20) KHz . This behavior reflects the transition from on process to another process, which may be related to a thermally activated charged particle in accordance with Maxwell – Wagner mechanism. This results in a monotonous decrease in the value of dielectric constant on increasing frequency for all the concentration. This observation may be attributed to a combined contribution to the dielectric constant due to electric, ionic, interfacial polarization at low frequencies. The resistance and resistivity values are higher at room temperature in the low frequency . A decrease in resistance and resistivity with rise in frequencies indicates a possibility of increase in the AC conductivity with increase frequency as shown in Fig .8&. The merger of real part of resistivity in the higher frequency domain suggests release of space charge and a consequent lowering of the barrier properties in the materials. The valence of added oxides has larger influence on the capacitance, resistance, dielectric constant, resistivity and conductivity values of fabricated semiconductors.

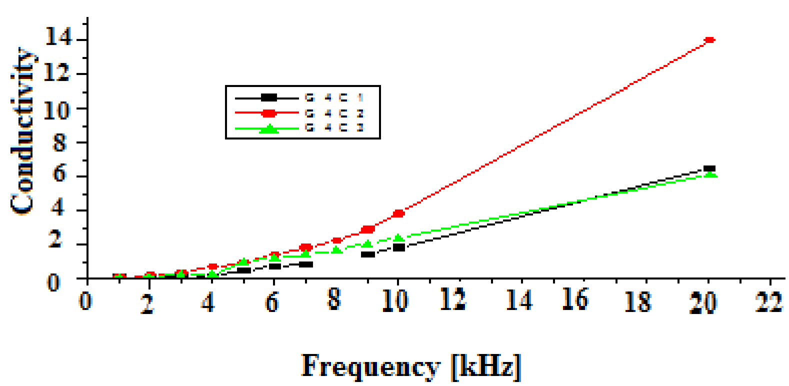


Fig .8. AC Conductivity as a function frequency for different mixes

References

Benko.F.A , 1981. p-TypeNiO as a Photoelectrolysis Cathode, J. Electrochem. Soc. 128,2476.

Bosman .A.J and C. Crevecoeur ,1966 . Mechanism of the Electrical Conduction in Li-Doped NiO. Phys. Rev. 144 , 763.

Botejue .J.C.N and TseungA.C.C, J. Electrochem.Soc. 1985.Preparation and characterization of NiO, Fe2O3, Ni0.04Zn0 . 132 ,2957.

Bruchez.M, Moronne.Jr.M, Gin.P, Weiss.S, and Alivisatos.A.P, 1998. Semiconductor Nanocrystals as Fluorescent Biological , Science, 2013,281.

Chan.W.C.W and Nie.S, 1998.Semiconductor nanocrystals and fluorescence microscopy.Science, 281, 2016 .

Chigane.M,Ishikawa.M,1998. Electrochromism and Electrochromic Devices. J. Chem. Soc., Faraday Trans. 94 , 3665.

Coe.S, Woo. W. K, Bawendi. M.G, and Bulovic.V,2002. Organic and Nanostructured Electronics, Nature (London) 420, 800 .

Colvin.V.L, Schlamp.M.C, and Alivisatos.A.P, 1994 Nanoparticles: From Theory to Application, Nature (London), 370, 354 .

Cook .J.G and Koffy berg .F.P, Solar Energy Mater. 10 (1984) 55.

Dabbousi . B. O ,Bawendi M. G, Onitsuka O , and Rubner .M. F, 1995 . Fluorescence intermittency in single cadmium selenide. Appl. Phys. Lett., 66, 1316 .

Gao.X and Nie.S, Trends Biotechnol, 2003.Multifunctional Quantum Dots for Personalized Medicine, 21, 371 .

He.H, Chang.Jr, Lao.S, Lih J. Chen, DragomirDavidovic, and Zhong L. Wang,2005 . Large-scale Ni-doped ZnO nanowire arrays and electrical and optical properties, J. Am. Chem. Soc. 127, 16376

Hotovy.I, Bue.D, Hascik S, Nennewitz.O,1998. Characterization and gas-sensing properties of nanocrystallineiron(III) oxide films prepared by ultrasonic spray pyrolysis on silicon, vacuum 50 , 41.

Hotovy.I,Rehacek.V,Siciliano.P,Capone.S, and Spiess.L, 2002.Sensing characteristics of NiO thin films as NO_2 gas sensor. Thin Solid Films 418, 9 .

Huynh.W.U, Dittmer.J.J, and Alivisatos.A.P, ,2002. Hybrid nanorod-polymer solar cells.Science, 295, 2425 .

Kadam.L.D, Bhosale.C.H, Patil.P.S , 1997 . On Spray Pyrolyzed Nickel Oxide Thin Films. Tr.J. Phys. 21 , 1037.

Kitao.M, Izawa.K, Urabe.K, Omatsu.T.K, Uwano.S.K, and Amada.S.Y,1994. Preparation and Electrochromic Properties of RF-Sputtered.Jpn. J. Appl. Phys. 33, 6656 .

Klimov.V.I, Mikhailovsky.A.A, Xu.S, Malko.A, Hollingsworth.J.A, Leatherdale.C.A, Eisler H.-J., and Bawend M. G.i, 2000.Optical gain and stimulated emission in nanocrystal, Science, 290,314.

Lampert, C.M., 1984. Solar Energy Mater.11 , 27.

Lampert.C.M, Omstead.T.R, Tu.P.C, Solar ,1986. Solar Energy Materials and Solar Cells,14,161.

Misho.R.H, Murad.W.A, Fatahalah .G.H, Abdul-Aziz.I.M, Al-Doon.H.M, 1988 Electrodepostion of nickel sulphate.Phys. Stat. Solidi (a) 109 ,K101.

Pramanik.P, Bhattachraya.S, 1990.Chemical Solution Deposition Of Semiconductor Films. J. Electrochem. Soc. 137, 3869.

Sato.H, Minami.T, Takata.S, and Yamada.T,1993. Thin Solid Films 236, 27 .

Seike.T, and Nagai.J,1991 . Proceedings of the Third Symposium on Electrochromic.Solar Energy Mater.22 , 107.

Surca. A, Orel .B ,Pilhar B ,. Bwkovec. P,1996. Preparation of Nickel Oxide Films by Anodizing .J. Electroanal. Chem. 408 ,83.

Tsu.R ,Esaki.L, Ludeke.R, 1969. Photoconductivity in Disordered Nickel-Oxide Films.Phys.Rev. Lett. 23 , 977.

Umagai.H.K, Matsumoto.M, T oyoda.K, and Obara.M ,1996 . J. Mater. Sci. Lett. 15, 1081 .

Utriainen.M, Kroger-Laukkanen.M, Niinisto.L, 1998.Ferromagnetic nanotubes by atomic layer deposition.Mater. Sci. Eng. B.54 , 98.

Varkey. A.J, Fort. A.F , 1993. Chemical Solution Deposition Of Semiconductor Films. Thin Solid Films 235 , 47.

Vincent C.A ,Bonion .F, Lizzari .M,andScrosati.B, 1987. Modern Batteries, 1st ed., Edward Arnold, London, (NiO) thin films - ResearchGate.6.

Wu.R.Q, Peng.G.W, Liu.L, and Feng.Y.P,2006. Phase transition mechanism in KIO_3 single crystals. Applied Physics Letters 89, 082504 .

Xie Yi., Wang .W, Qian.Y, Yang .Li., Chen.Z, 1996. Deposition and microstructural characterization of NiO thin films by a spray pyrolysis method. J. Cryst. Growth 167 , 656.

Zaban .A, Micic O. I. , Gregg. B. A, and Nozik .A. J, 1998. Annual Review of Nano Research.Langmuir 14 (12), 3153.