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Synthesis and Pressure Sensing Properties of the Pristine Cobalt Oxide Nanopowder

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During this study the pressure sensing properties of pristine Co_3O_4 nanopowder has been investigated. A transducer has been fabricated for the direct measurement of effect of pressure on impedance, capacitance and resistance of pristine nanopowders. On increasing pressure from 0 to 8.15 kN/m^2 the impedance and resistance of the samples reduces by 27% (on average) in the frequency range of 100 Hz to 200 kHz, while the capacitance increases by 58% at 100 Hz). It is also observed that the impedance of the samples decreases with increase in frequency. This behavior can be attributed to the densification of samples under the effect of pressure which intern reduces the porosity. Moreover, under the applied pressure the resistance (DC) initially rises with time and then saturates with-in 2-3 minutes. This phenomenon may be regarded to the effect of currents of bound charges (displacement current), including ions. The resistance- pressure relationship has also been simulated and the results found in good agreement with experimental data.

Keywords: Cobalt oxide nanopowder, Impedance; Pristine nanopowder; Pressure; Resistance; Transducer.

1. INTRODUCTION

Being a p-type semiconductor (magnetic) cobalt oxide is very active for the detection of carbon mono-oxide in the environment [1]. Cobalt oxide as an electrode material is extensively used for many applications such as electrochromic devices, glucose sensing lithium ion batteries, supercapacitors, water oxidation and cathode protection films [2]. The study of effect of pressure on the properties of materials is imperative for detail consideration of materials [3-5]. The organic semiconductor and conductor quasi one and two dimensional crystals have been studied under pressure for conductivity and thermoelectric power. It is concluded that the semiconductors' conductivity rises and thermoelectric coefficient reduces, while both the properties of conductors' remains more or less unchanged [6]. The metal-insulator transition in tetrathio-fulvalenium tetracyanoquinodimethane under the effect of pressure has also been studied [7]. Similarly, depending upon the study of material's (especially semiconductors) electrical properties different types of sensors can be fabricate [8]. Varity of sensors (like piezoelectric, resistance, capacitance and inductance sensors) with devices (such as bellows and diaphragm) are applied in pressure transducers [8, 9].

Zinc oxide (ZnO) thin film based pressure micro-sensor (piezoresistors) on a silicon substrate has been fabricated by Cardoso et al. [10]. These films had elastic modulus and electrical resistivity up to 156 GPa and 0.072ohm.cm, respectively; the high elastic modulus and low resistivity are the requisite for pressure sensors (piezoresistive). The resistance temperature coefficient and gauge factor of these piezoresistive sensors were -1610 ppm/K and 206 respectively. A ZnO single nano-wire based oscillator (nano-electromechanical) was fabricated by suspended nano-wire between two micro-machined metal electrodes and this oscillator showed better performance (electromechanical) in contrast to other formerly reported oscillators and may be implemented as sensors and actuators[11]. Chani et al. studied the pressure sensing properties of composite metal oxides nanosheets (oxides of Co, Zn and Fe) [12]. The results showed that the resistance (DC) and impedance reduced by 44% on applying 8.15 kN/m^2 pressure. The pressure sensing properties of tin oxide (SnO2) nanopowder were also studied and it was reported that the raise in pressure from 0 to 8.15 kN/m^2 resulted in reduction of impedance by 22% [13]. Karimov et al. fabricated a CNT-Cu_2O nanocomposite based pressure sensor [14]. The sensor was made by pressing composite powder in the tablet form, while the electric contact were made by silver paste. On applying pressure from 0-37kN/m2 the resistance (DC) of sensors reduced up to 3.3 times. The study of CNT-Cu_2O nanocomposite based strain sensors also showed that the strain sensitivity in compression was up to 28, while in compression was up to 46 [15]. Haniff et al. developed a pressure sensor on a flexible substrate by using Horizontally oriented CNTs (carbon nanotubes) [16]. It was found that on raising pressure from 0 to 50 kPa the performance of the sensors rise up to 1.68%/kPa.

Most of the sensors and physical experiments are based on thin films, pellets or crystals. Recently we studied the effect of pressure on the electric properties of pristine nanopowders by using a transducer [12, 13]. Our current study is based on the synthesis and pressure sensing properties of cobalt oxide (CO_3O_4) nano-powder (in pristine form)

2. EXPERIMENTAL

2.1. Synthesis of nanoparticles

All the chemicals (precursors and reagents) required for the synthesis of cobalt oxide (Co_3O_4) nanoparticles were purchased from Sigma Aldrich. Initially cobalt chloride aqueous solution (0.1M) was prepared and the pH of the aqueous solution was raised above 10 by adding NaOH solution (0.5

M). This high pH solution was put in a heat for a night which resulted in precipitation. The obtained precipitate were rinsed many times followed by drying and grinding. The final product was characterized in detail and then used for application.

2.2. Characterization

Field emission scanning electron microscope (JEOL, Japan) was used to analyze the morphology of Co_3O_4 nanoparticles. Elemental composition was analyzed with the help of Energy Dispersive Spectroscopy (Oxford). For bonding and crystal structure analysis of synthesized nanopowder the FTIR and Powder Diffractometer (ARLTM ARLX'TRA) with Cu K_α radiation (α =1.540 56 Å) were used, respectively.

2.3. Fabrication of transducer and testing of nanomaterial

A transducer has been fabricated for the direct measurement of effect of pressure on resistance, capacitance and impedance of samples (pristine nano-powder). Figure-1 shows the schematic diagram of the transducer, which is simple in design. The synthesized cobalt oxide (Co_3O_4) nanopowder with particle diameter of 40 nm on average is placed in cylindrical glass tube between metallic piston and the substrate made of stainless steel. The inner diameter of the tube and the outer diameter of the piston are 10 mm both, while the initial height of powder was equal to 0.2 mm and 0.7 mm for various samples. The rubber ring allows to minimize the effect of the environment (humidity and dust) on the performance of transducer. The pressure is inserted on the powder through the piston by applying load on it (Fig.1). As a result of applied pressure powder is squeezed between the substrate and the piston. The details of the arrangement for the measurement of effect of pressure on the electric properties of the materials are described by Karimov et al. [14]. During current study the load (Fig.1) was varied up to 0.64 N, that allow to create pressure up to 8.15 kNm^{-2}. The MT 4090 LCR meter (MOTECH) is used to measure the DC resistance and capacitance, impedance (in the frequency range of 100 Hz to 200 kHz).

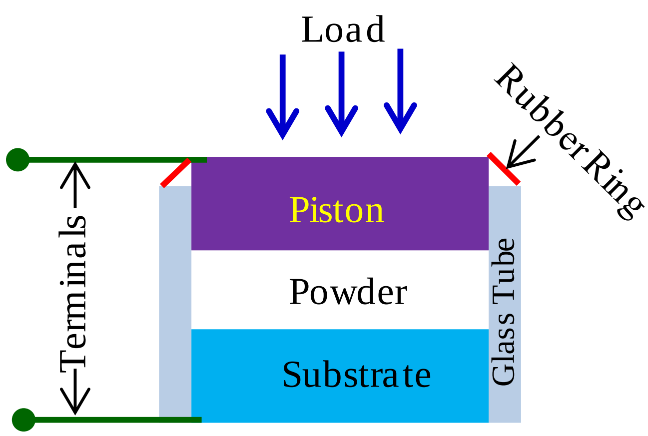

Figure 1. Schematic diagram of the fabricated transducer for investigation of resistance, impedance and capacitance of the pristine powder under pressure

3. RESULTS AND DISCUSSION

Fig. 2 shows the FESEM image of cobalt oxide nanopowder, which depict that the synthesized Co_3O_4 nanoparticles are spherical in shape with average diameter of 50±10 nm. The Co_3O_4 nanopowder is synthesized in large quantity.

The compositional analysis (EDS analysis) of the synthesized nanopowder is given in Fig.3. It is evident by the EDS spectrum that the synthesized nanopowder has only Co and oxygen and there is no other element as an impurity. The synthesis of pure cobalt oxide nanopowder is confirmed by the results of EDS analysis.

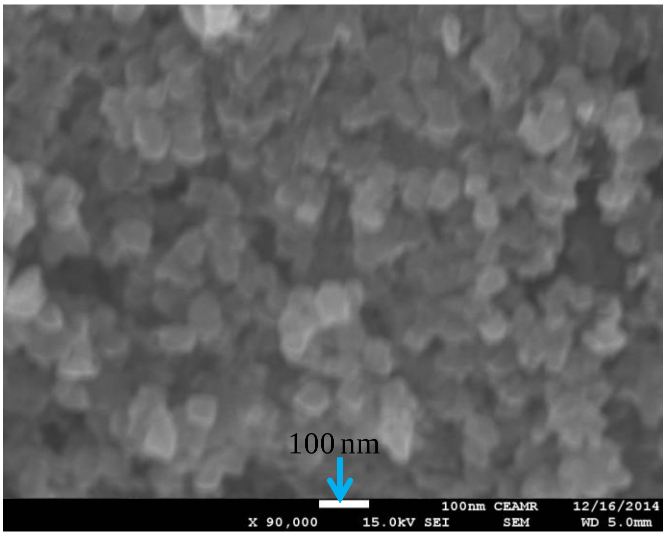

Figure 2. FESEM image of the synthesized cobalt oxide nanopowder

Element	Weight%	Atomic%
O K	33.43	64.91
Co K	66.57	35.09
Totals	100.00	

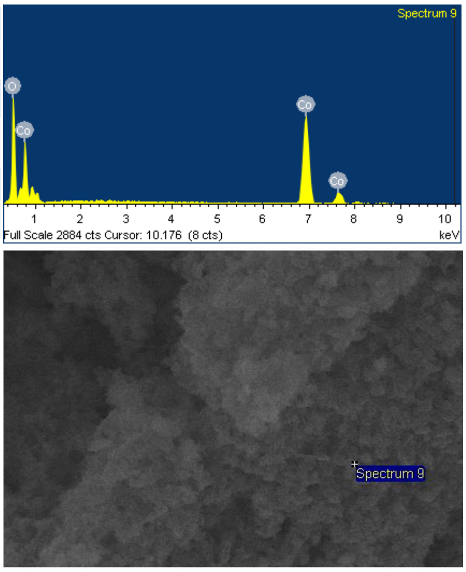

Figure 3. EDS analysis of the synthesized cobalt oxide nanopowder

The XRD pattern of cobalt oxide nanopowder is shown in Fig. 4(a), which illustrates the well crystalline peaks of Co_3O_4. The pattern of the nanoparticles shows a series of crystalline peaks which are well-matched with that given in literature for cobalt oxide (Co_3O_4) nanopowder [17]. Figure 4(b) shows the FT-IR spectra of synthesized Co_3O_4 nanopowder in which the absorption bands at 550 cm^{-1} and 660 cm^{-1} provides the clear evidence for the presence of Co_3O_4 crystals. Moreover, the stretching band at 1339 cm^{-1} indicate the presence NO_3 group.

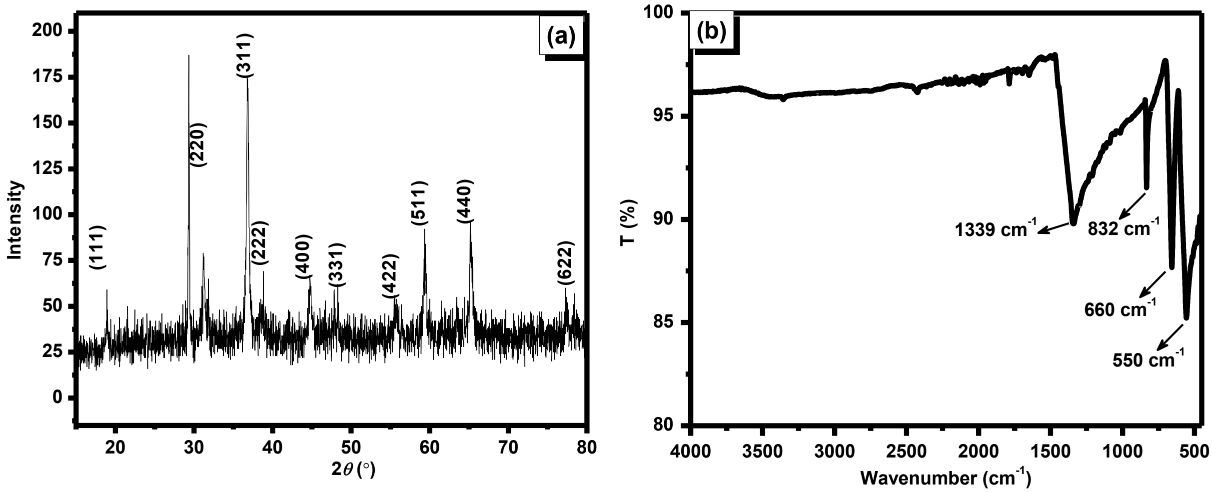

Figure 4. XRD (a) and FT-IR spectra of synthesized cobalt oxide nanopowder

Figure 5 shows the DC resistance-pressure relationship of the sample of pristine Co_3O_4 nanopowder having initial thickness of 0.2 mm, while the Fig. 6(a) and 6(b) respectively show the impedance-pressure and the capacitance-pressure relationships of the same sample at various frequencies (100 Hz to 200 kHz).

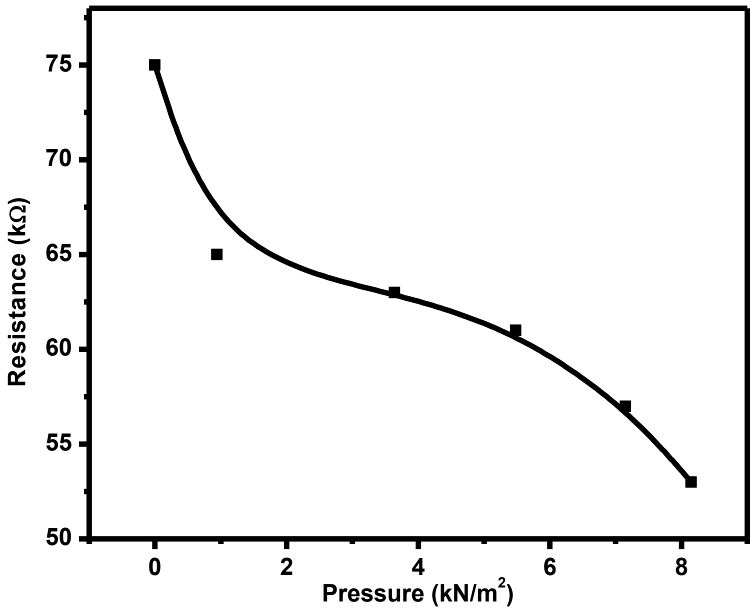

Figure 5. Resistance-pressure relationship of 0.2 mm thick cobalt oxide nanopowder sample

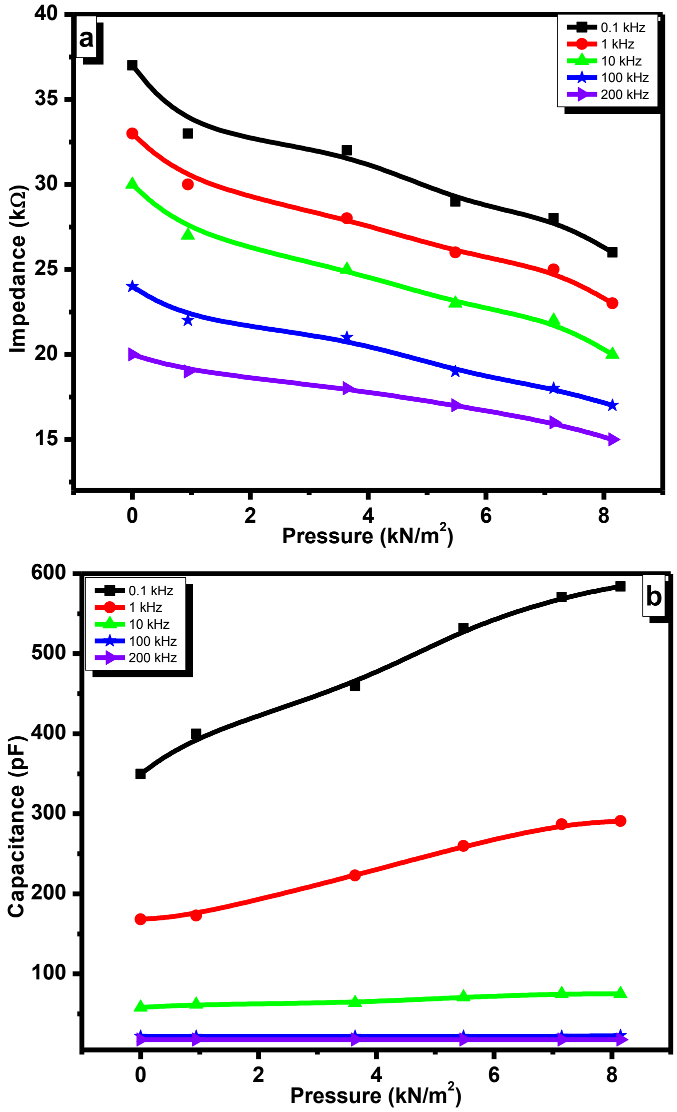

Figure 6. Impedance-pressure (a) and capacitance-pressure (b) relationships of 0.2 mm thick cobalt oxide nanopowder sample at various frequencies

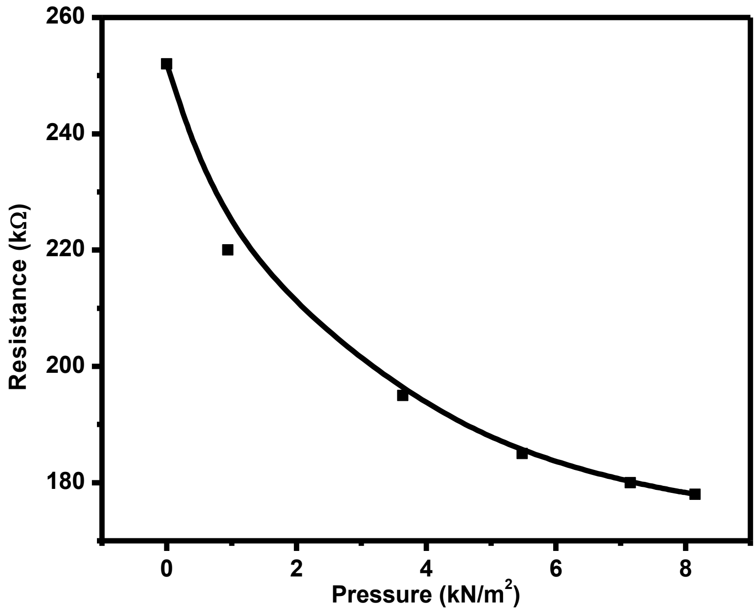

Figure 7. Resistance-pressure relationship of 0.7 mm thick cobalt oxide nanopowder sample

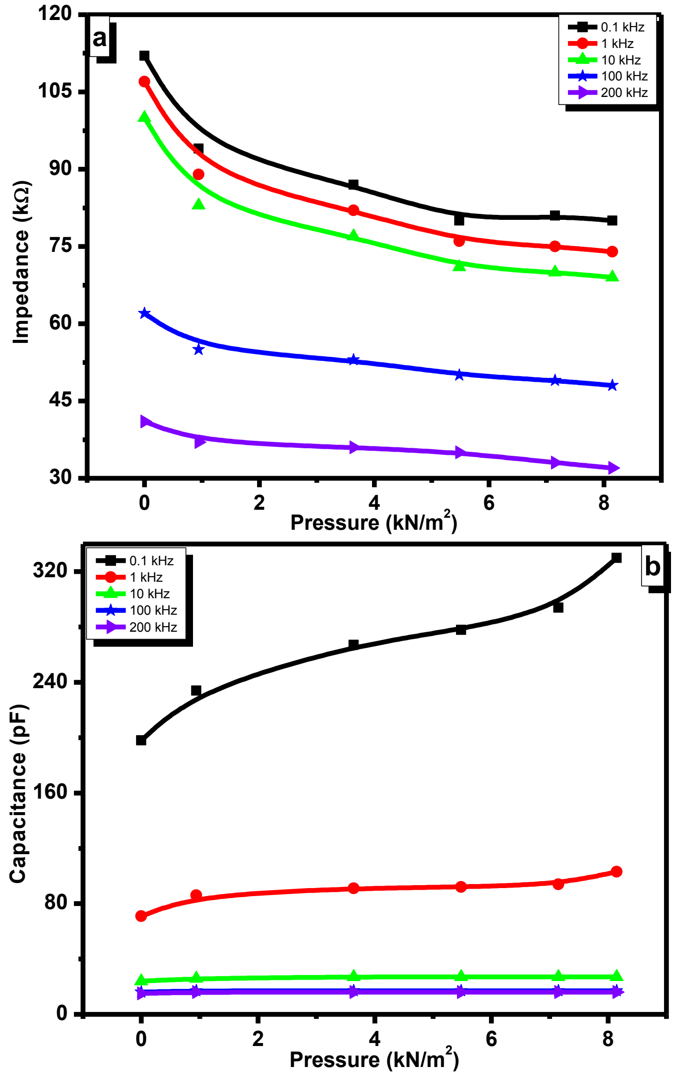

Figure 8. Impedance-pressure (a) and capacitance-pressure (b) relationships of 0.7 mm thick cobalt oxide nanopowder sample at various frequencies

The DC resistance-pressure relationship of the sample of pristine cobalt oxide nanopowder with 0.7 mm initial thickness is shown in Fig. 7, while its impedance pressure and capacitance-pressure relationships (at different frequencies) are shown in Fig. 8(a) and Fig. 8(b), respectively. From the above figures (Fig.5 to Fig.8) it can be seen that with increase in pressure the DC resistance and impedance of the samples decrease, while the capacitance decreases. By increasing pressure from 0 to 8.15 kN/m^2 the average decrease in DC resistance and impedance of the samples is 27%, while the average increase in capacitance is 58%. This decrease in resistance and impedance, and the increase in capacitance may be elucidated by powder's densification and reduction in porosity under the influence of pressure.

The resistance (*R*) of the transducer may be explained by using following expression [15, 18]:

$$R = {}^{d\rho}/_{A} = {}^{d}/_{\sigma A} \qquad (1)$$

In the above expression A and d are sample's cross-sectional area and inter-electrode distance or length, respectively, while ρ is the resistivity. The sample's (pristine Co_3O_4 nanopowder) initial conductivity was calculated as 3.46 10^{-7} Ω^{-1} cm^{-1} at room temperature conditions. The resistance-pressure relationships shown in Fig. 5 and Fig.7 may be regarded to the decrease of thickness (d) and reduction in porosity due to applied pressure, which consequently raises the conductivity (σ) of nanopowder.

The dependence of sample's resistance (DC) on time (pressure application time) is present in Fig.9. It can be seen (Fig.9) that the resistances (DC) increase with time and saturate after 2 to 3 minutes. This phenomenon may be considered by keeping in view the effect of well known displacement current of bound charges [19]. The resistance increases with time on average by 39% and 20% under pressure of 0 and 8.15 kN/m^2, respectively.

By the measurement of capacitance (C) of the sample the dielectric permittivity (ε) can be calculated [14, 18, 19]:

$$C = \varepsilon \varepsilon_0 A/d \tag{2}$$

where ε_o is the dielectric constant having value 8.85 10^{-12} F/m. It was found that the value of ε is 99.

Moreover, it is considered that the conduction mechanism of the samples (cobalt oxide nanopowder) is based on hopping transitions (thermally assisted) between particles or sites (spatially separated), which may be endorsed to Percolation Theory [20, 21]. On the base of this theory (Percolation Theory), the conductivity (average) may be determined by the following relationship:

$$\sigma = \frac{1}{LZ} \tag{3}$$

where Z the path resistance with lowest resistance (average) and L is the characteristic length (which depends on the concentration of sites). On increasing pressure first of all L decreases and subsequently Z also decreases. Consequently the increase in conductivity and decrease in resistance takes place; which was also observed experimentally (Fig. 5 and Fig.7).

The capacitance-pressure, impedance-pressure and resistance-pressure relationships can be simulated by using a following function [22]:

$$f(x) = e^{kx} \tag{4}$$

The modified form of the above function for capacitance-pressure relationship may be as follows:

$$\frac{C}{C_o} = e^{\Delta p k_1 2 p_m/(p_m+p)} \tag{5}$$

While for resistance-pressure relationship the above function (Eq.4) can be modified as follows

$$\frac{R}{R_o} = e^{\Delta p k_2 5 p_m/(p_m+4p)} \tag{6}$$

where C_o is initial capacitance and C is the instantaneous capacitance, while R_o and R are initial and instantaneous resistance, respectively. The Δp change in pressure, p is instantaneous pressure and the p_m is the maximum pressure. The k_1 and k_2 are the capacitance-pressure and resistance pressure factors, respectively and their values are 0.063 m^2/kN and -0.043 m^2/kN, accordingly.

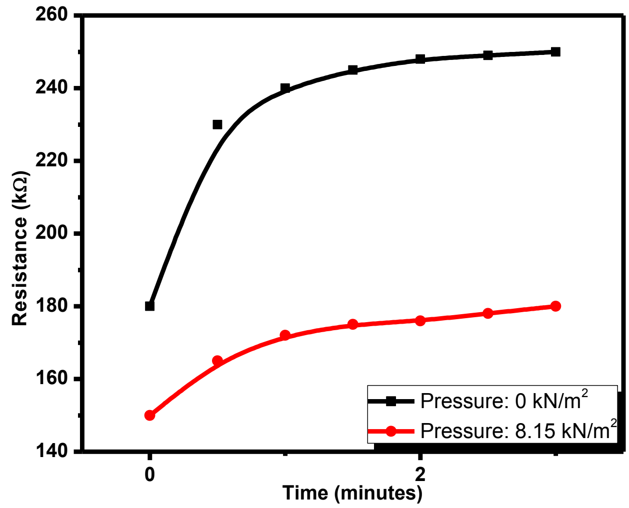

Figure 9. DC resistance-time relationship for the pristine cobalt oxide nanopowder at various pressures

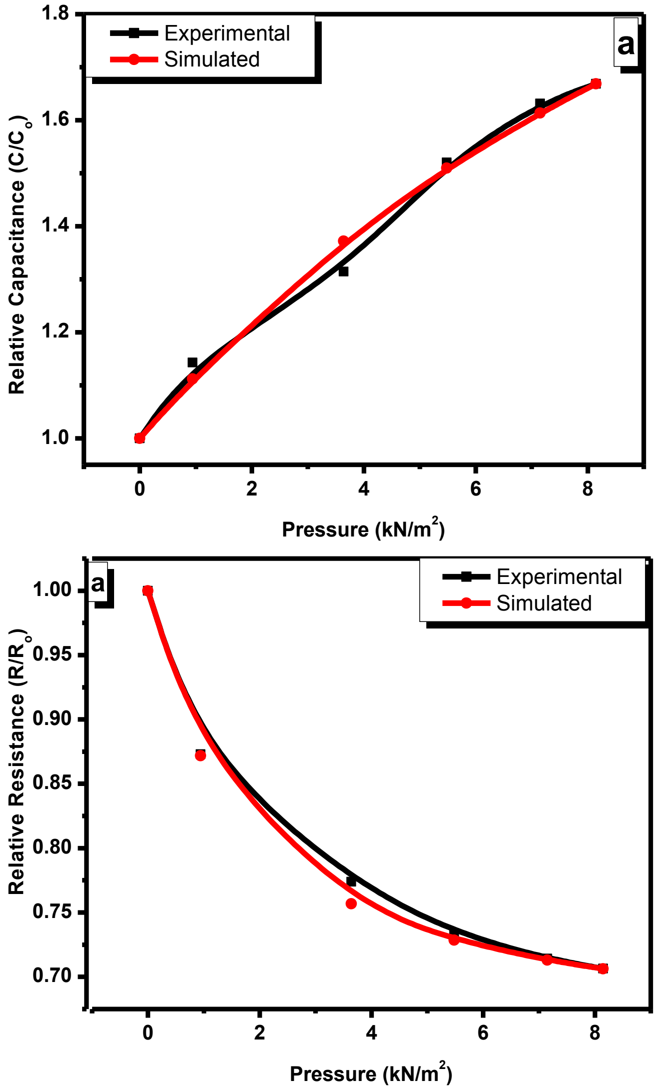

Figure 10. Comparison of simulated and experimental results for one of the capacitance-pressure (a) and resistance-pressure (b) relationships

The experimental and simulated results have been shown in Fig.10 (a and b): it is evident from the graphs that simulated results are comparable with experimental results. Same approach can be used to simulate the other results.

The parallel connected resistor and capacitor can be used to represent the equivalent electric circuit for nanopowder samples. The equivalent circuit diagram is shown in Fig.11 (a). It is evident from the circuit analysis and experimental results that with increase in frequency (*f*) the reactance ($1/2\pi fC$) reduces as compared to resistance. With increase in pressure the reactance reduces comparative to resistance at lower frequency but increases at higher frequencies. Conduction takes place through the nanoparticles; the capacitance current through pores and the displacement current of bound charges through the nanoparticles.

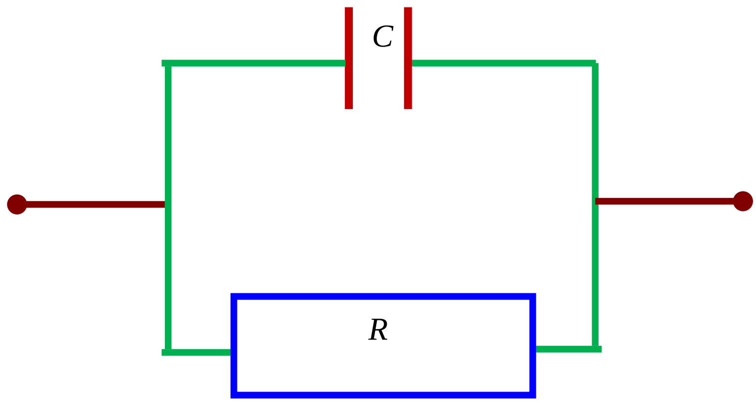

Figure 11. Equivalent electric circuit of the nanopowder samples

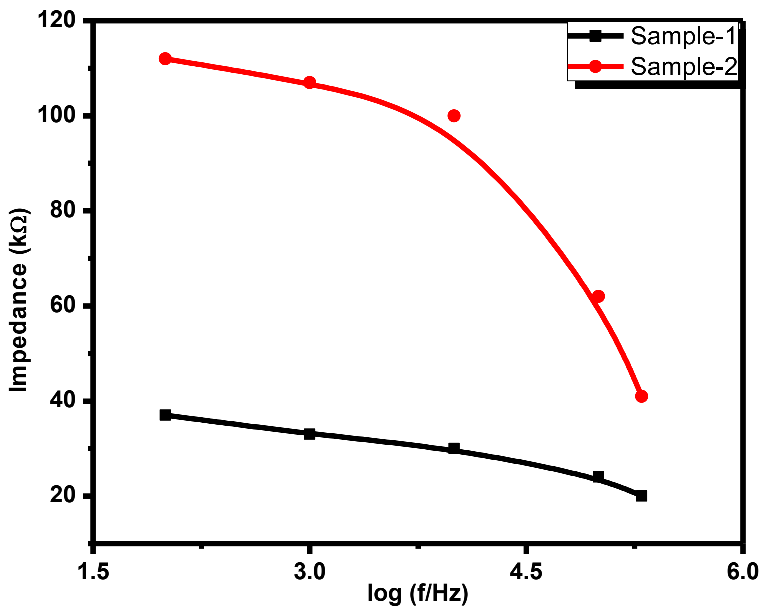

Figure 12. Impedance-frequency (*f*) relationships of cobalt oxide nanopowder obtained by using results shown in Fig.6(a) (sample-1) and Fig.8(a) (sample-2)

The circuit presented in Fig.11 looks suitable for nano-powder's samples and conductive micro-units that are comprised of two neighboring nanoparticles. The confirmation of this circuit is done by the experiment: the impedance-frequency relationships shown in Fig.12 are obtained from the data presented in Figs. 5(a) and 7(a) for both type of samples (0.2 mm and 0.7 mm thick). It can be seen from Fig.12 that impedance decreases with increase in frequency and the data presented in this Fig. is comparable with the results obtained on CuO nanofibres earlier [23]. The detailed description of the physical aspect of the obtained results will be presented elsewhere.

4. CONCLUSION

A transducer has been fabricated to measure directly the effect of pressure on the capacitance, impedance and the resistance pristine nanopowders. Cobalt oxide nanopowder was investigated for pressure sensing and it was revealed that on increasing pressure from 0 to 8.15 kN/m^2 the impedance and resistance reduced by 27% on average in the frequency range of 100 Hz to 200 kHz. It is observed that under applied pressure resistance initially raises and then saturates within 2 to 3 min. The capacitance of the samples at 100 Hz increased by 58% on average. The prepared samples are considered as parallel connected resistor and capacitor in which conduction take place through resistors (nanoparticles) and capacitors (micro-pores). Change in pressure and/or frequency may results in change in “resistance” and “capacitance” and consequently in impedance. The capacitance-pressure and the resistance-pressure relationships have been simulated and the results of simulations are comparable with the experimental results.

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References

1. C.Y. Liu, C. F. Chen and J.P. Leu, *Electrochem. Solid-State Lett*., 12 (2009) J40-J43.
2. J. Wang, C. Wu, K. Wu, Q. Cheng and Y. Zhou, *Analy. Chim. Acta*, 736 (2012) 55-61.
3. M. Brahmia, B. Bennecer and A. Hamidani, *J Phys. Chem. Solids*, 74 (2013) 1336-1340.
4. M.B. Kanoun, S. Goumri-Said, A.E. Merad, G. Merad, J. Cibert and H. Aourag, *Semicond. Sci. Technol.*, 19 (2004) 1220.
5. F. S. Saoud, J. C. Plenet and M. Henini, *Physica* B, 407 (2012) 1008-1013.
6. K.S. Karimov, Electrophysical properties of low-dimentional organic materials at deformation, Department of Heat Physics, Academy of Sciences, Tashkent, Uzbekistan, 1993.
7. C.W. Chu, J.M.E. Harper, T.H. Geballe and R.L. Greene, *Phys. Rev. Lett.*, 31 (1973) 1491-1494.
8. J.W. Dally, W. Riley and K.G. McConnell, Instrumentation for engineering measurements, John Wiley and Sons Inc., New York, 1993.
9. C.D. Simpson, Simpson (1996) Industrial electronics, Prentice Hall (Englewood Cliffs, NJ)1996.
10. G.W.A. Cardoso, G. Leal, A.S.d. Silva Sobrinho, M.A. Fraga and M. Massi, *Materials Research*, 17 (2014) 588-592.
11. G.-R. Zhou, H.-B. Lv, X.-D. Yuan, H. Zhou, H. Liu, K.-X. Li, X.-F. Cheng and X.-X. Miao, *Chin. Phys. Lett.*, 32 (2015) 034202.

12. M.T.S. Chani, K. Sher Bahadar, S.K. Kh, M. Abid, M.A. Abdullah and A. Kalsoom, *J. Semicond.*, 36 (2015) 023002.
13. M.T.S. Chani, S.B. Khan, A.M. Asiri, K. Karimov, M. Abid, M.M. Bashir and K. Akhtar, *Optoelectron. Adv. Mater.-Rapid Commun.*, 9 (2015) 114-119.
14. K.S. Karimov, M.T.S. Chani, F.A. Khalid, A. Khan and R. Khan, *Chin. Phys*. B, 21 (2012) 016102.
15. K.S. Karimov, M.T. Saeed Chani, F. Ahmad Khalid and A. Khan, *Physica* E, 44 (2012) 778-781.
16. M.A.S.M. Haniff, H.W. Lee, D.C.S. Bien, A.S. Teh and I.A. Azid, *Nanoscale Res. Lett*., 9 (2014) 1-5.
17. S. Farhadi, J. Safabakhsh and P. Zaringhadam, *J. Nanostruct. Chem*., 3 (2013) 1-9.
18. M.A. Omar, Elementary Solid State Physics: Principles and Applications, Pearson Education (Singapore) Pt. Ltd., Indian branch, Delhi, India, 2002.
19. D.V. Sivukhin, Physics, Electricity, Nauka, Moscow, 1977.
20. H. Bottger, V.V. Bryksin, Hopping conduction in solids, VCH, Deerfield Beach, FL, (1985).
21. C. Brabec, V. Dyakonov J. Parisi and N.S. Sariciftci, Organic Photovoltaics: Concepts and Realization, Springer-Verlag, Berlin Heidelberg, 2003.
22. A. Croft, T. Croft and R. Davison, M. Hargreaves, Engineering mathematics: a modern foundation for electronic, electrical, and control engineers, Addison-Wesley1992.
23. G.N.S. Vijayakumar, M.Rathnakumari and P.S. Kumar, *Arch. Appl. Sci. Res.*, 3 (2011) 514-525.