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Ni-SiO$_2$ Nano Composite as a MISFET Gate Dielectric and Electrochemical Impedance Spectroscopy Investigation for This Process

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NiO-SiO$_2$ can be used in a variety of devices, such as in circuit boards and detectors, including odor sensors, due to its porous structure. Owing to these specific properties, these composites attract the attention of many researchers. To study the effect of Ni-nano particles on NiO-SiO$_2$ composition, we have demonstrated a series of experiments to synthesize different size and structured shape of NiO-SiO$_2$ composition. The methods of sol-gel with using XRD (X-ray Diffraction), SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy) techniques are used to determine the optimum conditions of obtaining composition and getting good gate dielectric for the future of MISFET (Metal- Insulator- Semiconductor- Field- Effect- Transistor) devices. The obtained results show that increase in silicon oxide content and synthesizing temperature change the composite structure, in that an amorphous structure (or nanoscale crystallites) with 4:1; NiO:SiO$_2$ may be considered as an alternative gate dielectric. In continuous, the effect of NiO-SiO$_2$ composition on charge transfer resistance (R_{ct}) investigated with using electrochemical impedance spectroscopy (EIS) method in the presence of 1 mM $K_4[Fe(CN)_6]$ material. Result also shows that NiO-SiO$_2$ composition can reduce electrical conductivity electrode and increase charge transfer resistance in the presence of 1 mM $K_4[Fe(CN)_6]$.

Keywords: Nano powders, Nano composite, Sol-gel method and XRD technique.

1. INTRODUCTION

Nanotechnology has become one of the most interesting disciplines in science and technology today [1-8]. The intense interest in nanotechnology is being driven by various interesting fields and is leading to a new industrial revolution. Nano-materials such as nanoparticles, or nanocomposite connected with other molecular are being used for several bioanalytical and dielectric applications [8,9-12].

One device most widely used is silicon-based integrated circuits is the MOSFET (Metal-Oxide-Semiconductor-Field-Effect-Transistors) [12-15]. However, the success of the device attributes to several technologically important factors. First, silicon can be thermally oxidized to produce a stable oxide which is an excellent insulator [14]. Second, the surface-state density at the silicon-oxide interface is sufficiently low to ensure reproducibility [16]. Third, being planner, the structure is amenable to large-scale integration [17]. However, some issues such as boron diffusion through the ultra-thin, increased leakage current and limit the use of ultra-thin silicon for the next CMOS (Complementary Metal Oxide Semiconductor) devices.

Therefore it will be interesting to investigate and found an alternative gate dielectric with higher gate dielectric constant (high-k). NiO can fill this gap.

We have thus demonstrated the series of experiments to provide a good dispersion of nano Ni as well as NiO particles in SiO_2 and studied the nano structured properties of nano composite NiO-SiO_2 with using XRD (X- Ray Diffraction), SEM (Scanning Electron Microscopy) and TEM (transmission Electron Microscopy) techniques. The obtained results indicate that NiO-SiO_2 composite with amorphous structure (NiO:SiO_2; 4:1, produce at 200°C), higher dielectric constant, higher quality factor (measured with GPS 132A technique), surface free cracks and compacted structure can be introduced as a good candidate of the next nano electronic devices. Furthermore, from the electrochemical point of view, in cyclic voltammetry, chronoamperometry and especially electrochemical impedance spectroscopy (as powerful techniques for studying electron transfer in electrical systems [14-20]), we found that the cited nano composite can affect charge transfer resistance on carbon paste electrode (more details will be discussed in the future).

2. EXPERIMENTAL PROCEDURES AND DETAILS

The sol-gel process is commonly applied to synthesis such NiO materials owing to its several advantages such as low temperature processing and the ability to prepare materials in various shapes, compared with the conventional preparation procedures of glass and ceramics. The materials used for the synthesis were: $Ni(NO_3)_2$, $6H_2O$ (Merck), NaOH , ethylene glycol (p.a.), ethanol (C_2H_5OH) and Tetra Ethyl Ortho Silicate(TEOS) (Fluka,98%). The metallic nitrates, weighed to the designed stoichiometric ratio, have been dissolved in ethyleneglycol and ethanol. The obtained solution has been slowly added in drops, while stirring, to the above solutions. Ethanol has been added in order to increase the miscibility of the two solutions. The homogenous, clear solutions obtained in this synthesis were subordinated to stirring at room temperature and air atmosphere to jellify. After 24h stirring, the sol was changed to gel. The obtained gels have been dried in the drying - oven at 80 ºC, for 15 minutes. After drying and milling, the resulted powders have been thermally treated at different temperatures (200^o C – 500 ^{o} C) with 10- 30 wt% Ni nano particles in SiO_2 matrix and then characterized.

In parallel to above studies, we interested in particle behavior at gate dielectric and electrode contact as, to say, a particle sensor (more details will be presented in the future). This idea causes a motivation to study electrochemical behavior of the sample. For preparation of the electrode in EIS study a 10.0% (w/w) nanocomposite modified carbon powder was made by dissolving the given quantity of $NiO\text{-}SiO_2$ in diethyl ether and hand mixing with 90.0 times its weight of graphite powder with a mortar and pestle. The solvent was evaporated by stirring a mixture of 10.0% wt $NiO\text{-}SiO_2$ modified carbon powder. Paraffin oil was added to the mixture and blended by hand-mixing. The resulting paste was inserted in the bottom of a glass tube (with internal radius 3.0 mm). The electrical connection was implemented by a copper wire lead fitted into a glass tube. A carbon paste electrode without $NiO\text{-}SiO_2$ was prepared in the above procedure.

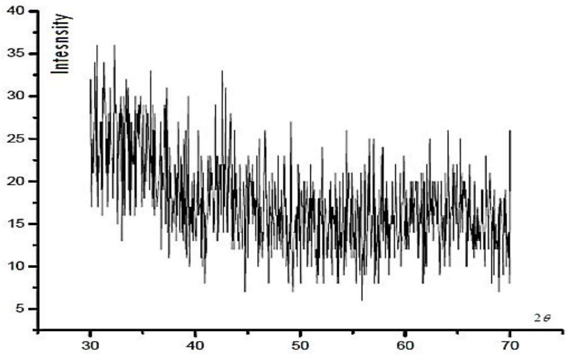


Figure 1. X-ray diffraction pattern of the $NiO:SiO_2$; 4:1 composite at 200^{o}C.

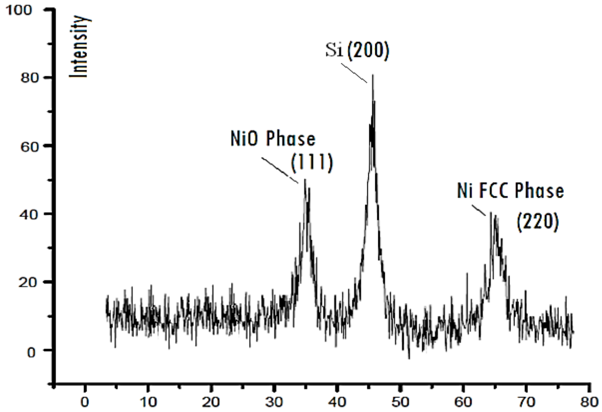


Figure 2. X-ray diffraction pattern of the $NiO:SiO_2$; 4:2 composite at 350°C. There are NiO, Si and Ni FCC phases.

The structural evolution of samples is characterized by XRD, TEM and SEM techniques. The phase composition of the $NiO\text{-}SiO_2$ films is studied with using XRD technique. The XRD patterns are obtained with using $Cu_{k\alpha}$ ($\lambda = 1.5406 A^{\circ}$) source, with scanning at a rate of $1^{o}\ \min^{-1}$ for 2θ ranging from 10^{o} to 80^{o} . Figures 1-3 show XRD patterns of NiO- SiO_2 composite obtained by sol- gel method. As shown in figure 1, the sample prepared at 200 °C with $NiO:SiO_2$; 4:1 is nearly amorphous. In figures 2 and 3, it has crystallization structure at 350°C (with $NiO:SiO_2$; 4:2) and 500 °C (with

$NiO:SiO_2$; 4:2). As shown in figure 2, peaks located at 37°, 44° and 64-67° attributed to the NiO (111), Si(200) and Ni (220) crystallite phases. By increasing temperature of composite (compare figure 2 to 3), there are no changes in NiO, Si and Ni FCC phases (just better crystalline structure are appeared in figure 3) due to formation of crystallites attributed to the lower surface energy, which is important in the nucleation of crystals.

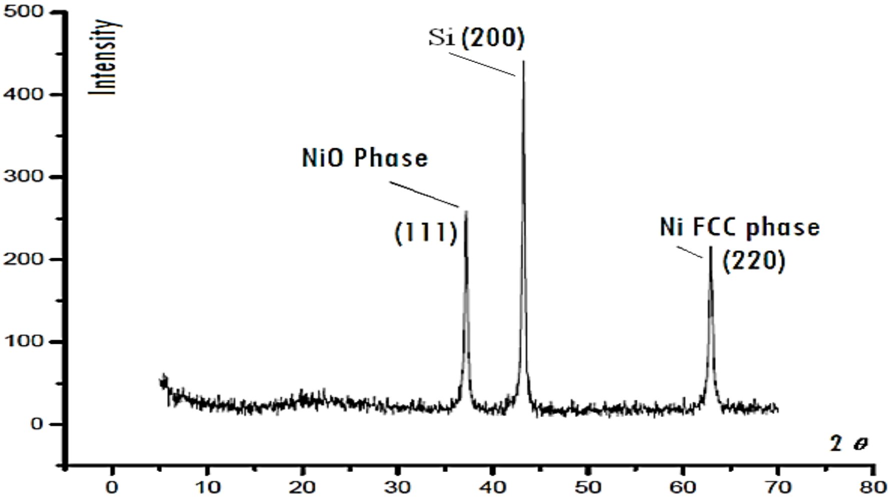
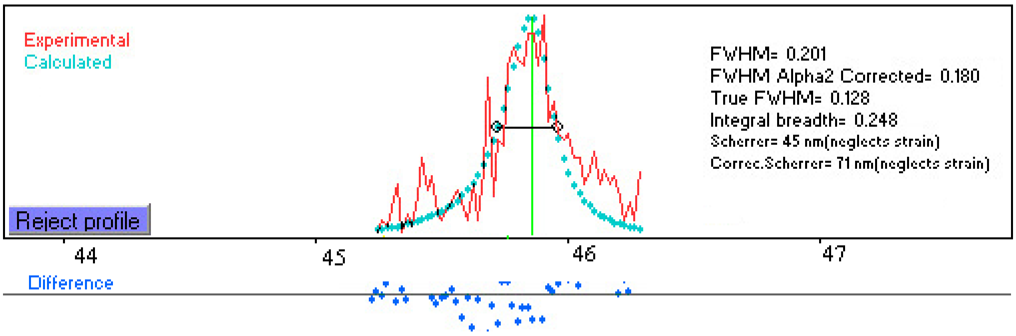


Figure 3. X-ray diffraction pattern of the $NiO:SiO_2$; 4:2 composite at 500°C. There are still NiO , Si and Ni FCC phases

The average nanocrystallite size can be deduced from Scherer equation [21]:

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad \textbf{(1)}$$

Where D is the crystallite size, k_α is a constant (0.94), λ is the wavelength of X-ray ($Cu_{k\alpha}$ = 1.5406Å), β is the true half- peak width, and θ is the half diffraction angle of the centered of the peak in degree.



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FWHM= 0.201
FWHM Alpha2 Corrected= 0.180
True FWHM= 0.128
Integral breadth= 0.248
Scherrer= 45 nm(neglects strain)
Correc.Scherrer= 71 nm(neglects strain)
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Figure 4. X-powder method has been used for determining Ni particle size in $NiO:SiO_2$; 4:2 composite synthesized at 350°C. The size of Ni nano crystallite synthesized at 350°C is 45 nm

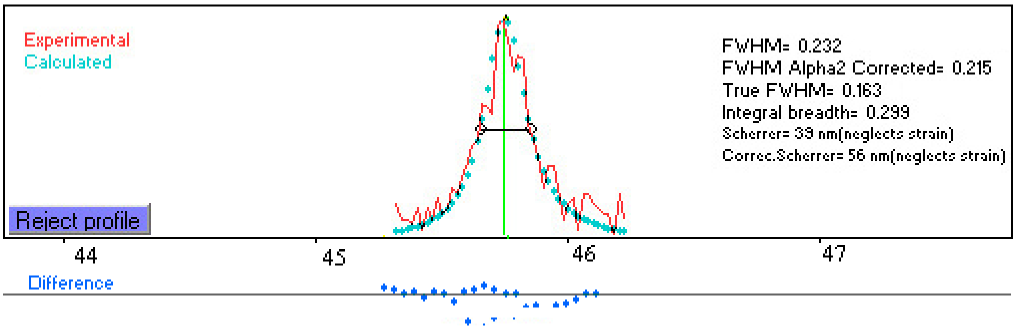

Figure 5. X-powder method has been used for determining NiO particle size in NiO:SiO_2; 4:2 composite synthesized at 500°C. The size of Ni nano crystallite synthesized at 500°C is 33 nm

X- Powder software has also been used to measure the crystallite size (Scherer equation can be applied for spherical crystallites). The results estimated by Scherer equation and X- powder software (corrected Scherrer) are given in figures 4 and 5 (data inserted in these figures). It is clear that there is no accurate size measurement for NiO:SiO_2; 4:2 composite at 200°C due to its amorphous structure.

In addition to XRD studies, SEM has routinely been used to investigate the morphology of the nano-particles. The morphology of the sample surface in SEM image (figure 6) shows the presence of amorphous structure at 200ºC, but adding more Ni and/or NiO nano particles as well as further heating up to 500ºC (figure7), there is a transformation of amorphous composite to microcrystalline structure.

Figure 6. SEM image of the NiO:SiO_2; 4:1 composite at 200°C. There is no crystallite phase.

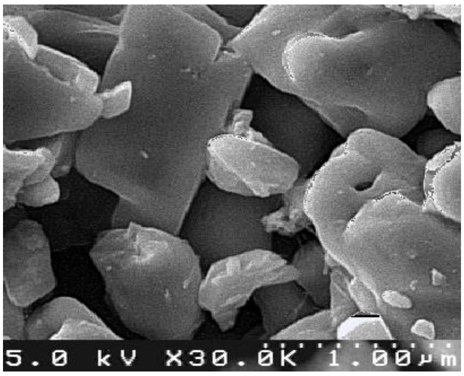

Figure 7. SEM image of the NiO:SiO_2; 4:2 composite at 500°C. There are micro crystallites.

TEM images in figures 8 and 9 confirm above claims. Figure 8 shows an amorphous phase at 200^{o}C. The dark region in figure 8 (synthesized at 200^{o}C), represents the agglomeration of amorphous NiO, which changed to same needle-form tubes at higher temperature at 500ºC, as shown in figure 9. Crystallizes directly from amorphous to NiO, Si (SiO_2) and Ni FCC phases at 350 and 500°C, one appeared after heating the sample.

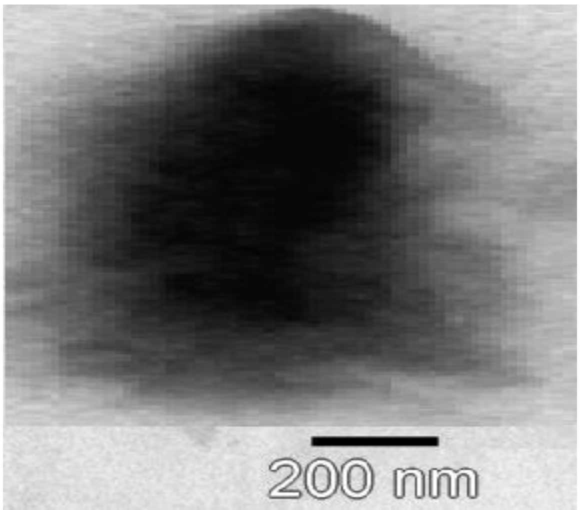

Figure 8. TEM image of the NiO: SiO_2; 4:1 composite at 200°C. It is amorphous structure.

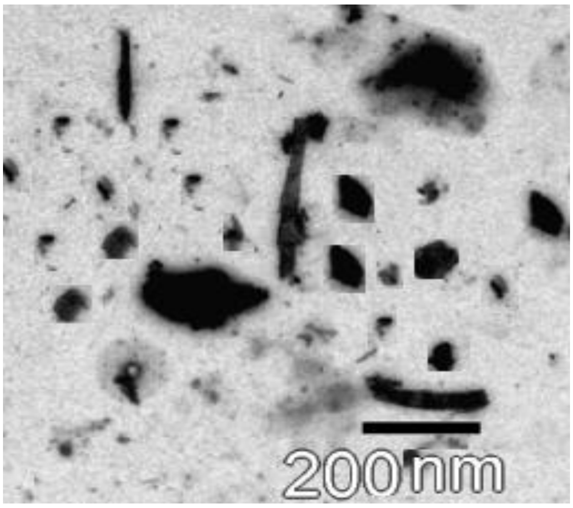

Figure 9. TEM image of the NiO:SiO_2; 4:2 composite at 500°C. There are nano crystallites.

To study the electrical properties of the presented samples, we used GPS 132 A. By fabricating parallel plate capacitors and using LCR meter (model; GPS 132 A), the capacity (c) has been measured. Consequently the dielectric constant has been calculated using the following equation:

$$C = K\frac{A\varepsilon_0}{d}$$

Where C is the measured capacitance, ε_0 (=8.85 x 10^{-12} ($F \cdot m^{-1}$)) is the permittivity of free space, A (=1.2 Cm^2) is the area of the capacitor and d (= 3 mm) is the thickness of the dielectric, in that K can be determined.

The electrical resistivity of the films decreases with the Ni and O contents as measured with GPS 132 A. As can be seen in table 1, Self Inductance (L), Resistor (R), Capacitance (C), Dielectric Constant (k), Quality Factor (Q_F) and Dissipation Factor (D_F) are obtained for NiO:SiO_2; 4:2 composie and calcinated temperatures 200- 500°C.

Dielectric constant, electrical resistence and quality factor of the sample synthesized at 200°C are higher than those at 500°C synthesized temperature, which could be due to dipole moments vector amplification in former sample. Higher Q_F indicates a lower rate of energy loss relative to the stored energy of the capacitor as follow

$$Q_F = 2\pi \times \frac{\text{Energy Stored}}{\text{Energy dissipated per cycle}}$$

D_F is a measure of loss-rate of energy of capacitor and can vary depending on Ni crystallite size, the dielectric material and synthesized temperature. It is the reciprocal of Q_F as:

$$D_F = 1/Q_F$$

Table 1. *L*, *C*, *R*, *k*, Q_F and D_F of NiO measured with GPS 132 A.

Sample	*L* (H)	*C* (pF)	*R* (MΩ)	*k*	Q_F ($=1/D_F$)
As-prepared	107.1	18.2	2.3	20.11	0.41
200 ˚C	329.5	27.5	2.7	39.62	5.61
500 ˚C	1423.1	13.9	1.9	16.26	3.26

It is clear that from 200°C to 500°C, the value of *k* decreases, whilst D_F value increases. Mathematically, the expression for current density according to Poole–Frenkel model [22] can be written as:

$$J = AT^2 \exp \frac{1}{k_B T}\left[\left(\frac{57.7\ eV}{Kd}\right)^{1/2} - \varphi_t\right]$$

where, K is the dielectric constant of the film, *d* is electrode spacing in Å, φ_t is the depth of the trap potential well and *A* is the Richardson constant having a value of 120 A/cm^2K^2. It demonstrated a lower tunneling or leakage current for higher dielectric constant, so it can reduce tunneling current as well and leakage current.

3. RESULTS AND DISCUSSION

Figures 1, 2 and 3 show NiO:SiO_2; 4:1 and NiO:SiO_2; 4:2 composites and different synthesized temperatures. It is clear that an increase about 10wt% Ni and/or NiO in the content of silicon dioxide in the samples, the amorphous structure changed into micro crystallite structure. We found that the NiO peaks get narrower at higher temperature and grow with respect to the amorphous silica background. Although the intensity of NiO and Ni-FCC phases in figure 3, increases significantly, the NiO/Ni intensity ratio is the same. The broadening of NiO and Ni peaks at lower temperature (350^{o}C) indicate that the mean crystallite size reduces for NiO:SiO_2; 4:2, from 45 to 33 nm (as measured with X- Powder software).

The reduction of particle size could be due to reduction the specific surface area of the samples and suppressing the processes of sintering of the nanodispersed nickel phase.

It can reduce leakage and tunneling current due to its amorphous structure Figure 4 shows NiO/SiO_2 nano component is amorphous at low temperature (200ºC) due to large number of Ni- SiO_2 interfacial polarization.

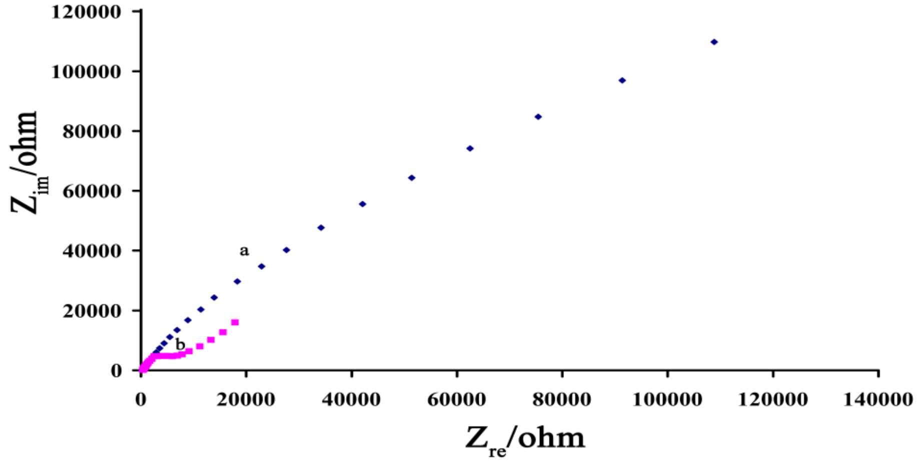

Figure 10. Nyquist diagrams of carbon paste electrode modified with NiO:SiO_2 (a); Nyquist diagrams of unmodified carbon paste electrode modified. Condition: frequency range of 100 kHz to 1.0 Hz; the AC voltage amplitude used was 5 mV; in the presence of 1 mmol L^{-1} $K_2Fe(CN)_6$.

As stated above, we made a capacitor, like gate/ gate dielectric/ substrate: Al/ NiO+ SiO_2/ Si and measured some key parameters as dielectric constant, quality factor with GPS 132 A and the obtained results are given in table 1. Upon heating the nano composites at 350ºC- 500ºC, NiO as well as SiO_2 get crystalline form. The higher dielectric constant (k= 39.62), quality factor (Q_F= 5.61), Self conductance, resistance (R) and capacity (C) for NiO:SiO_2; 4:2 nano composite synthesized at 200^{o}C is more than those others, meaning this composite can be used as a good gate dielectric for the future of CMIS (Complementary Metal Insulator Semiconductor) devices.

On the other hand, electrochemical impedance spectroscopy is a powerful and very informative technique for probing charge transfer properties at the electrode–solution interface [18]. We have used electrochemical impedance spectroscopy to study NiO:SiO_2 nanocomposite to evaluate their charge transfer coefficients. The values of the charge transfer coefficients have direct relation with electron transfer in electro active materials [19-20]. The compounds with high charge transfer coefficient are suitable for preparation of MISFET gate dielectric. Figure 10 shows the Nyquist diagrams of the imaginary impedance (Zim) vs. the real impedance (Zre) of the EIS obtained at the carbon paste electrode which includes NiO:SiO_2 in the presence of 1 mM $K_4[Fe(CN)_6]$. They have been recorded at 0.45 V dc-offset in 1 mM $K_4[Fe(CN)_6]$. Result shows that the charge transfer coefficient in the presence of NiO:SiO_2 (curve a) is bigger than that of the charge transfer coefficient in the absence of it (curve b). This result shows thatNiO:SiO_2 can be used a suitable and good MISFET gate dielectric.

4. CONCLUSION

The higher dielectric constant (k= 39.62), quality factor (Q_F= 5.61), higher charge transfer coefficient and capacity (C) for NiO:SiO_2; 4:1 nano composite synthesized at 200^oC can be used as a good gate dielectric for the future of CMIS (Complementary Metal Insulator Semiconductor) devices. Finally, electrochemical impedance spectroscopy was used as a powerful technique for investigation of this nanocomposite.

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