Annealing temperature effect on structural and optical investigations of Fe$_2$O$_3$ nanostructure

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**Abstract**

Ferric oxide (Fe$_2$O$_3$) was synthesized at different temperatures ($T_\text{S}$) between 300 and 500 °C by spray pyrolysis technique. Surface of annealed Fe$_2$O$_3$ nanostructure was characterized by field emission scanning electron microscopic (FESEM). Annealed Fe$_2$O$_3$ nanostructure has showed rhombohedral hexagonal structure with the preferred orientation along (104) plane in X-ray diffraction patterns (XRD). Crystallite size was increased from 43 to 63 nm with increasing of $T_\text{S}$ between 300 and 500 °C. The maximum transmittance was found to be 72% for Fe$_2$O$_3$ nanostructure at $T_\text{S} = 300$ °C. The energy gap for direct band transitions was measured to be 2.05−2.09 eV. Refractive index of Fe$_2$O$_3$ nanostructure in the visible region was found in the range of 2.37−2.62. Fe$_2$O$_3$ nanostructure has showed n-type electrical conductivity and electrical resistivity was found in the range of 1.02 × 10$^4$−6.23 × 10$^4$ Ω m. Formation of transparent Fe$_2$O$_3$ nanostructure with band gap and high refractive index suggests the suitability of Fe$_2$O$_3$ nanostructure in gas sensors.

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1. Introduction

Nowadays semiconductor metal oxide nanoparticles are attractive due to their differences in electric, dielectric, optical, bio-medical, photo-catalytic and magnetic properties respect to their same bulk counterparts [1–5]. α-Fe$_2$O$_3$ is very popular due to its non-toxicity, less costly, abundance, thermal and chemical stability at ambient temperature and environmentally friendly [6–9]. It is an intrinsically n-type semiconductor with rhombohedral crystal structure, high refractive index and direct band gap around 1.9 and 2.2 eV [10]. Fascinating properties of α-Fe$_2$O$_3$ makes it suitable for various electronic and optoelectronic applications like gas-sensors, vapor...
sensors, microwave devices, high-density recording media, solid state lithium ion batteries, supercapacitors, water splitting for hydrogen production, solar cells and antibacterial coating [11,12]. \(\alpha\)-Fe\(_2\)O\(_3\) is synthesized by several techniques as successive ionic layer adsorption and reaction method [10], sol–gel [12] and chemical vapor deposition [13] to report the optical and structural properties of \(\alpha\)-Fe\(_2\)O\(_3\) nanostructure via aqueous solution of Fe(NO\(_3\))\(_3\)·9H\(_2\)O varied with \(T_S\) and deposition time.

Yadav et al. [14] have prepared electrochemical supercapacitor performance Hematite \(\alpha\)-Fe\(_2\)O\(_3\) by spray pyrolysis from non-aqueous medium. They have studied structural, morphological optical and electrochemical properties of \(\alpha\)-Fe\(_2\)O\(_3\). They have revealed that \(\alpha\)-Fe\(_2\)O\(_3\) has well covered nanoporous surface. The as prepared films exhibited a direct band gap energy varying from 2.36 to 2.14 eV. The \(\alpha\)-Fe\(_2\)O\(_3\) has showed a maximum specific capacitance 451 F g\(^{-1}\) within potential window –1.1 to 0.2 V in aqueous 2 M KOH electrolyte. Such nanoporous \(\alpha\)-Fe\(_2\)O\(_3\) with high performance may be used as a promising material for electrochemical supercapacitors. Hierarchical oxide nanostructure had proved by Jia et al. [15] a promising feature in gas sensing due to their high surface areas and well-aligned nanoporous structures containing less agglomerated configurations. They have developed a facile method to prepare Ag/\(\alpha\)-Fe\(_2\)O\(_3\) microspheres using \(\alpha\)-FeOOH microspheres as precursor and AgNO\(_3\) as Ag resource. Their results revealed that Ag nanoparticles with diameter 5 nm formed on the surface of hollow \(\alpha\)-Fe\(_2\)O\(_3\) spheres were composed of primary nano-sized particles. The addition of Ag served as an active catalyst, creating more active sites believed crucial for enhancing sensitivity. Li et al. [16] have observed two modulated structures caused by long-range ordering of oxygen vacancies in \(\alpha\)-Fe\(_2\)O\(_3\) nanowires (NWs) produced after oxidation of Fe. Both types of oxygen vacancy ordering structures have a similar modulation periodicity of 1.45 or 1.50 nm with corresponding atomic ratios of Fe and O (Fe/O) of 0.7407 and 0.7273, respectively. They have studied electron energy-loss spectroscopy to show the Fe/O ratio of NWs is close to that of Fe\(_2\)O\(_4\) when oxygen atoms are not sufficient, which makes the NWs energetically favorable.

Although various studies have been performed, but still there is a lot of studies of effect of annealing temperature on specific properties of \(\alpha\)-Fe\(_2\)O\(_3\) nanostructure. Spray pyrolysis technique (SPT) is simple and less expensive technique for preparation of dense and uniform nanostructure via a simple chemical route. There are various deposition parameters such as precursor, solvent concentration, substrate temperature (\(T_S\)), spray rate, pressure of carrier gas and nozzle to substrate distance. \(T_S\) is necessary parameter since growth kinetics strongly depends on the temperature at which pyrolysis occurs. Effect of \(T_S\) on the properties of \(\alpha\)-Fe\(_2\)O\(_3\) nanostructure has been reported by few researchers [14–16].

The morphology of annealed Fe\(_2\)O\(_3\) nanostructure prepared at various \(T_S\) captured at ×30K magnification is represented by FESEM images as shown in Fig. 1. FESEM images are comprised of clusters of nanoparticles and film surface and getting roughness with rising \(T_S\) from 350 to 500 °C. Increasing of surface roughness may be associated with the fact that film growth kinetics is governed by chemical reaction in vapor state of spray solution at higher \(T_S\) [17]. After annealing the Fe\(_2\)O\(_3\) nanostructure, nanoparticle agglomerates to be more distinguishable as observed in Fig. 1. Among the four FESEM images, Fig. 1(a) represents uniformity and even distribution of nanoparticles on the film surface; the reason of uniformity may be attributed to removal of oxide layers and rearrangements of particles via annealing process. This is may be due to the temperature effect [18–20]. The surface morphology of Fe\(_2\)O\(_3\) nanostructure deposited at \(T_S\), 400 °C is not much

2. Experimental process

Spray pyrolysis reactor was used for preparation of \(\alpha\)-Fe\(_2\)O\(_3\) nanostructure 0.1 M aqueous solution of iron (III) chloride hexahydrate (FeCl\(_3\)·6H\(_2\)O, purity 99% MERCK, Germany). The precursor salt was dissolved in distilled water by stirring the mixture with a magnetic stirrer for 60 min in order to acquire a homogeneous solution and a few drops of ethanol was added to the solution to ensure better crystallinity. The pH value of solution was about 4. Ultrasonically and chemically cleaned glass slides were used for deposition. An ebonite spray gun with outlet aperture diameter, 0.001 m was utilized. The nozzle for substrate separation was arranged constant at 25 cm during process of spray. The air has used as carrier gas and air pressure was maintained at 0.50. Spray rate was kept constant at 5 mL/min during deposition. \(\alpha\)-Fe\(_2\)O\(_3\) was deposited for 10 min at various \(T_S\) between 300 and 500 °C. \(\alpha\)-Fe\(_2\)O\(_3\) nanostructure was annealed at 450 °C for 60 min in a tubular furnace (Carbolite SHEFFIELD, UK). The surface morphology of \(\alpha\)-Fe\(_2\)O\(_3\) nanostructure was studied by field emission scanning electron microscope (FESEM) (JEOL JSM-7600F, Japan). The FESEM images were taken at 30,000 (×30K) magnification.

The structure of annealed \(\alpha\)-Fe\(_2\)O\(_3\) nanostructure was monitored by X-ray powder diffractometer (XRD, PANalytical EMPIREAN SERIES 2, Netherlands) for wavelength, 1.5406 Å as Cu Kα operated target in power input, 60 kV. “X’Pert Highscore“ computer software was utilized to research 2θ values, spacing of interplanar (d) value and FWHM is full width at half maximum. These parameters of structure were compared with standard data of \(\alpha\)-Fe\(_2\)O\(_3\) (JCPDS card: 24-0072). Optical transmittance and absorbance of \(\alpha\)-Fe\(_2\)O\(_3\) nanostructure were tested at ambient temperature via UV–vis spectrophotometer (Dynamica Halo DB-20, Australia) in the wavelength range, 200–1100 nm.

3. Results and discussion

3.1. Structural properties

The morphology of annealed Fe\(_2\)O\(_3\) nanostructure prepared at various \(T_S\) captured at ×30K magnification is represented by FESEM images as shown in Fig. 1. FESEM images are comprised of clusters of nanoparticles and film surface and getting roughness with rising \(T_S\) from 350 to 500 °C. Increasing of surface roughness may be associated with the fact that film growth kinetics is governed by chemical reaction in vapor state of spray solution at higher \(T_S\) [17]. After annealing the Fe\(_2\)O\(_3\) nanostructure, nanoparticle agglomerates to be more distinguishable as observed in Fig. 1. Among the four FESEM images, Fig. 1(a) represents uniformity and even distribution of nanoparticles on the film surface; the reason of uniformity may be attributed to removal of oxide layers and rearrangements of particles via annealing process. This is may be due to the temperature effect [18–20]. The surface morphology of Fe\(_2\)O\(_3\) nanostructure deposited at \(T_S\), 400 °C is not much
changed due to low annealing process for removal of fine cracks. At $T_5$, 400, 450 and 500 °C, the particle agglomerates and found more clearly visible as seen in Fig. 1(b), (c) and (d), respectively. Fig. 1(d) exhibits the nanoparticle-agglomerates to be more closely spaced on the film surface, porous and forming a rock-like morphology. It can be said that the surface roughness of annealed Fe$_2$O$_3$ nanostructure is found to be increased with $T_5$. Similar annealing effect on surface morphology is observed for Fe$_2$O$_3$ nanostructure [21]. The surface morphology of Fe$_2$O$_3$ nanostructure is observed of porous nature which is strongly influenced by $T_5$ and annealing. Response of Fe$_2$O$_3$ nanostructure-based gas sensor depends very strongly on the surface morphology [22].

XRD patterns of annealed $\alpha$-Fe$_2$O$_3$ nanostructure in Fig. 2 show improvement in polycrystalline rhombohedral hexagonal crystal structure with the peaks (104), (110), (006), (300), (122). Among all these peaks, (104) is the predominant one indicating high orientation along that crystal plane. The XRD patterns are matching the standard data of $\alpha$-Fe$_2$O$_3$ (JCPDS card: 24-0072) [23]. No peak corresponding to non-stoichiometric or any other phase of $\alpha$-Fe$_2$O$_3$ is found. Intensity of (104) peak increases with increasing of $T_5$ and indicating the betterment of crystallinity of $\alpha$-Fe$_2$O$_3$ nanostructure via annealing which is in good agreement with other [23,24]. The intensity of (104) peaks is rising with the rise of $T_5$. The other peaks are appearing in XRD patterns of annealed $\alpha$-Fe$_2$O$_3$ nanostructure in an irregular manner. This may be affirmed as the difference in surface morphological features as shown in Fig. 1.

Crystallite size ($D$) and dislocation density ($\delta$) of $\alpha$-Fe$_2$O$_3$ nanostructure have been evaluated by Scherrer formula [25].

\[
\text{Porosity (\%) } = 1 - \left( \frac{\rho_{\text{exp}}}{\rho_{\text{std}}} \right) \times 100
\]

The strain ($\varepsilon$) and lattice constants ($a$ and $c$) of $\alpha$-Fe$_2$O$_3$ nanostructure are calculated using the relations given in the references [26,27], respectively. Texture coefficient ($T_C$) for the preferential (104) peak in the XRD pattern of $\alpha$-Fe$_2$O$_3$ nanostructure is evaluated using the equation mentioned elsewhere [28]. Porosity of $\alpha$-Fe$_2$O$_3$ nanostructure is computed using the relation [29].
Table 1 – Structural parameter of annealed α-Fe₂O₃ nanostructure.

<table>
<thead>
<tr>
<th>Tₛ (°C)</th>
<th>D (nm)</th>
<th>ε 10⁻⁴</th>
<th>δ 10⁻⁴ (nm⁻²)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>Tc (104)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>43</td>
<td>9.22</td>
<td>6.90</td>
<td>5.0157</td>
<td>13.8334</td>
<td>2.76</td>
<td>0.36</td>
<td>0.30</td>
</tr>
<tr>
<td>350</td>
<td>44</td>
<td>9.08</td>
<td>6.87</td>
<td>5.0217</td>
<td>13.8013</td>
<td>2.75</td>
<td>0.38</td>
<td>0.35</td>
</tr>
<tr>
<td>400</td>
<td>45</td>
<td>8.57</td>
<td>5.95</td>
<td>5.0120</td>
<td>13.6957</td>
<td>2.73</td>
<td>0.43</td>
<td>0.67</td>
</tr>
<tr>
<td>500</td>
<td>63</td>
<td>7.13</td>
<td>4.39</td>
<td>5.0312</td>
<td>13.6775</td>
<td>2.72</td>
<td>0.52</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 2 – Optical properties of annealed α-Fe₂O₃ nanostructure.

<table>
<thead>
<tr>
<th>Tₛ (°C)</th>
<th>Eₑ (eV)</th>
<th>η (at 650 nm)</th>
<th>k (at 650 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.090</td>
<td>2.37</td>
<td>0.16</td>
</tr>
<tr>
<td>350</td>
<td>2.084</td>
<td>2.38</td>
<td>0.17</td>
</tr>
<tr>
<td>400</td>
<td>2.076</td>
<td>2.54</td>
<td>0.21</td>
</tr>
<tr>
<td>500</td>
<td>2.058</td>
<td>2.62</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Fig. 3 – Variations of transmittance (T%) of annealed Fe₂O₃ nanostructure.

where ρₑxpt and ρₑtd are the experimental and standard density of α-Fe₂O₃. Table 1 presents the structural parameters of annealed α-Fe₂O₃ nanostructure. Increasing of D with Tₛ can be correlated directly as found in FESEM images. Decreasing of ε and δ values with rising of Tₛ occurs as a consequence of rising D value. There is an increasing in a value excepting for case at 400 °C and decreasing in c value, followed by c/a ratio reduces indicating a reduction of size of unit cell and lowering the growth along c-axis. Rise of Tc (104) is a strong evidence of promotion of growth along (104) plane. Increment in porosity of annealed α-Fe₂O₃ nanostructure may occur as a result of removal of oxide layers and rearrangements of particles via annealing that correlate directly. D values of annealed α-Fe₂O₃ nanostructure are found in few nm, which is very much suitable for gas sensing applications. Small particle size ensures large specific surface area and excellent sensitivity to gases [30].

3.2. Optical properties

Optical transmittance (T) of annealed α-Fe₂O₃ nanostructure is plotted against photon wavelength as displayed in Fig. 3. The annealed α-FeO nanostructure is found transparent in UV-vis. In Fig. 3, T increases slightly with increasing of Tₛ in the range 300–500 °C. Maximum T is found to be 72% for α-Fe₂O₃ nanostructure deposited at the Tₛ, 300 °C. Clearer porosity at low Tₛ is more effective than high Tₛ and corresponding to small D, that causes an increasing of T as proved in Table 1. Reduction in T of α-Fe₂O₃ nanostructure deposited at Tₛ, 500 °C may be attributed to higher surface roughness and changes in the structure and morphology [31].

Fig. 4 – Tauc plots of annealed α-Fe₂O₃ nanostructure.

Extinction coefficient (k) is calculated using the formula [32] as displayed in Table 2. The optical band gap for direct transition (Eₐ) is calculated using Tauc formula [33] and refractive index (η) is evaluated using the formula [32]. Eₐ of annealed α-Fe₂O₃ nanostructure is evaluated using the Tauc plots as shown in Fig. 4. Eₐ value decreases with increasing Tₛ which may be attributed to the change in surface morphological and structural features. Band gap values are in accordance with values of α-Fe₂O₃ [2,14].

4. Conclusions

The structure, morphology and optical properties of α-Fe₂O₃ nanostructure synthesized at different Tₛ in the range of 300–500 °C are investigated by SPT. Annealed hexagonal rhombohedral structure is highly improved with enhancement of intensity of (104) peak in XRD patterns, the porous structure is more regulated with increasing of roughness. The annealed α-Fe₂O₃ nanostructure was transparent. Optical band gap, refractive index and extinction coefficient of annealed α-Fe₂O₃ nanostructure correlated inversely and directly with Tₛ, respectively. The α-Fe₂O₃ nanostructure deposited at Tₛ, 500 °C shows less transmittance, high refractive index and high extinction coefficient due to its high roughness. It can be stated that highly absorbing, better crystalline structure
and porous surface of α-Fe₂O₃ nanostructure are possible to achieve at Tₛ, 300 °C. It is expected that α-Fe₂O₃ nanostructure is a suitable candidate for gas sensors.

Conflicts of interest

The authors declare no conflicts of interest.

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