Nonlinear-Electronic Transport in Fe$_2$O$_3$ Thin-Films Grown from Grain-Oriented Iron Foils

Roberto Baca Arroyo

Department of Electronics, National Polytechnic Institute, Distrito Federal, Mexico City 07738, MEX, Mexico

Correspondence should be addressed to Roberto Baca Arroyo; rbaca02006@yahoo.com.mx

Received 16 August 2013; Accepted 24 October 2013

Academic Editor: Feng Zhao

Copyright © 2013 Roberto Baca Arroyo. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Nonlinear-electronic transport in Fe$_2$O$_3$ thin-films grown by thermal oxidation from grain-oriented iron foils was studied by current-voltage characteristics at room temperature as a function of the oxidation temperature. Microstructure formation and its changes were investigated by atomic force microscopy and X-ray diffraction studies. X-ray diffraction has demonstrated that average grain size was weakly increased with the growth temperature. The analysis of current-voltage characteristics shows ohmic regime at low voltages and space-charge-limited regime at higher voltages. Space-charge effects resulted from the discontinuous grain growth of the foils. Further, nonlinear-electronic transport of Fe$_2$O$_3$ thin-films can be useful for the designing of adaptive oxide electronic devices.

1. Introduction

Space-charge-limited current was studied in vacuum tube technology at around 1906. Scientists had developed technologies based on vacuum tubes including high-power, signal amplifier, and military applications, due to its resistance to electromagnetic pulse. Therefore, the space charge phenomena can renewal the era of solid-sate-electronics in the operation principle of adaptive oxide electronic devices based on space-charge effects, which could be useful for smart devices with nonlinear characteristics [1–3].

Recently was demonstrated how changing from bulk to nanoscale materials can significantly change the material properties in transition metal oxides (TMOs) [4] and consequently their performance. Therefore, space-charge effects at the interface between small particles can result in substantial improvement of the electrical, magnetic, and optical properties [5–7].

Adaptive oxide electronic devices based on vertical structure with small area can be implemented in driver circuits for power applications [8, 9], because the current flow can be modulated by an electrode embedded in the middle of the device even for low carrier mobility of the metal oxide thin-films [7, 10]. Also, in response to the needs of ecological concerns, low-cost, abundance, stability, nontoxicity, and environmentally, TMOs should be studied and adapted for new applications. For example, iron oxide has attracted interest of researchers [11–13]. It is well known that hematite (Fe$_3$O$_4$) has a low conductivity as well as low electron mobility at room temperature in comparison with silicon [14]. Also, it is known that activation energy for Fe$_2$O$_3$ varies nonmonotonically with temperature [15, 16].

Nonlinear-electronic transport in Fe$_2$O$_3$ thin-films produced by thermal oxidation has been investigated in this work. Microstructure formation was studied by atomic force microscopy and X-ray diffraction as a function of the growth temperature as well as the study of the nonlinear-current conduction as a function of thickness was conducted by current-voltage characteristics at room temperature.

2. Experimental Procedure

Fe$_2$O$_3$ thin-films were grown by thermal oxidation from grain-oriented iron foils. The grain-oriented iron foil is a soft magnetic material that is used as the core material in electrical transformers. In this work, grain-oriented foils were obtained from cores of low-power transformers with thickness of
0.18 mm. It is known that grain-oriented foils are usually coated to reduce the eddy currents and to provide resistance to corrosion. Therefore, before oxidation processes, the iron foils with cross-sectional area of 1 cm² were mechanically polished and cleaned using organic solvents and deionized water. After polishing, the samples were thermally oxidized under air atmosphere conditions in the temperature range from 400 C to 550 C with duration of 20 min into resistively heated quartz tube furnace. A copper electrode of square geometry of 0.1 cm × 0.1 cm was placed on each sample as mechanical point contact as shown in the schematic diagram of Figure 1.

Microstructure formation was analyzed by both atomic force micrographs and X-ray diffraction patterns. Atomic force micrographs of the Fe₂O₃ thin-films were obtained with a Digital Instrument (Veeco) Nanoscope and X-ray diffraction patterns with a PANalytical X-ray diffractometer with CuKα radiation (λ = 0.15418 nm) in the scan range 20–90°. Current-voltage characteristics of the samples were measured by using digital storage oscilloscope (Tektronix, TDS1012C). Both voltage and current signals were plotted as lissajous figures on the screen of oscilloscope. A lissajous figure gives the instantaneous values of voltage as a function of the current.

3. Results and Discussion

It is known that the oxidation process of iron oxide should be dependent on the solubility of oxygen into iron foil and energy to take an oxygen ion and form the oxide. Therefore, vacant cation sites (oxygen ions) will diffuse away from the oxide-air interface and vacant anion sites (iron ions) through the oxide during the oxidation process [17]. In the procedure presented here at intermediate temperature (<700°C), a first monolayer of oxide is grown and corresponds to Fe₃O₄ phase with lattice parameter similar to grain-oriented iron foil. This phase is characterized by a Goss texture with a (110) preferred crystal orientation [18].

Then, the oxide continues to grow with this texture with strong cohesive forces [17, 19]. Structural defects can be formed into the grown oxide by discontinuous Goss grain growth, which is depending on the industrial production process of the grain-oriented iron foils.

3.1. Microstructure Formation. Microstructure formation studies are conducted to know the stability of the Fe₂O₃ thin-films grown by thermal oxidation at lower temperature than 700°C and under air atmosphere conditions. Atomic force microscopy studies were done to demonstrate the homogeneity and reproducibility of the samples controlled by diffusion process and X-ray diffraction analysis to show the polycrystalline Fe₂O₃ phase formation in the samples.

Figure 2 shows the atomic force micrographs of Fe₂O₃ thin-films at various temperatures. A noncontact mode of operation was employed between the tip and sample with scanned area of 1 μm × 1 μm to provide a method to analyze the oxide formation on samples surface as a function of the roughness based on bearing algorithm from Veeco Nanoscope software.

The average roughness, R̄avg, can be estimated with the intersection of both depth profile and bearing area plots as indicated in Figure 3 with dashed lines and is related to average grain height distribution, and their values are presented in Table 1.

It is demonstrated that a discontinuous growth mechanism favors the oxide formation and grain size in the samples as shown in Figure 3. However, at temperatures (>500°C), a decrease of the oxide formation can be observed in Figure 3(d), because the discontinuous oxide achieves its critical thickness [17, 18, 20].

Figure 4 shows X-ray diffraction patterns of the thermally oxidized samples. Samples were processed at 400°C and 450°C with peaks located at 65.08° and 81.07° with (530) and (710) planes. Samples were processed at 500°C with peaks located at 30.06°, 35.46°, 43.02°, 65.04°, and 81.07° corresponding to (220), (311), (400), (530), and (710) planes as well as peaks positioned at 33.13°, 35.53°, 42.98°, 65.04°, and 81.07° with (310), (311), (400), (530), and (710) planes.
were observed in samples processed at 550°C. All peaks correspond to the cubic Fe$_2$O$_3$ phase according to PANalytical Card no. 00-019-0629. The cubic Fe structure can be seen in all samples processed with peaks at 44.67° and 82.33° with (110) and (211) planes according to PANalytical Card no. 00-002-0426 and associated with Goss texture [18].

The thickness $d$ of samples was measured by a Tencor profilometer. Both thickness $d$ and average grain size $D$ were indicated in Table 1. Average grain size was estimated with Debye-Scherrer formula based on X-ray diffraction patterns [21, 22].

According to atomic force microscopy studies of Figure 3 and X-ray diffraction analysis of Figure 4, the main scattering mechanism for carries in Fe$_2$O$_3$ thin-films can be grain boundary scattering, which is associated with transitional regions between different orientations of neighboring crystallites. Also, potential barrier between crystallites with lattice defects-induced trapping states can impede the carrier motion into the Fe$_2$O$_3$ thin-films. As a consequence, when the mean free path of carriers is comparable with smaller crystalline sizes, $D$, and critical thickness, $d$, the charge carrier mobility, $\mu$, could be limited according to microstructure data of Table 1 for Fe$_2$O$_3$ thin-films.

3.2. Electronic Transport. The performance of samples was demonstrated with the schematic diagram of Figures 1(a) and 1(b). To ensure the linear response, a function generator (Matrix, MFG-8250A) was used to produce a linear ramp signal at low frequency ($f = 100$ Hz) with voltage range from 0 V to 5 V to conserve low-voltage operation and avoid magnetic transport (exchange polarization) in the samples [23, 24]. Also, a resistor of $R = 100$ Ω was selected to monitor the current signal in the samples as shown in Figures 1(a) and 1(b). Current-voltage characteristics for both forward

![Atomic force micrographs of the oxidized samples under air atmosphere conditions.](image-url)
and reverse bias are shown in Figures 5 and 6. Nonlinear-electronic transport was observed on the current-voltage characteristics with two regions indicated by slopes.

To investigate the transport parameters of the samples, a model of space-charge-limited transport was proposed and given by

\[ I = \frac{9}{32\pi\varepsilon \mu A_e} N_c N_i \exp\left(-\frac{\phi_i}{k_B T}\right) \frac{V^n}{d^3}, \]

(1)

where \( \varepsilon \) is the iron oxide dielectric constant (taken as \( \varepsilon = 540 \) for \( \text{Fe}_2\text{O}_3 \) at low frequencies) [15], \( k_B \) is the Boltzmann constant, \( T \) is the sample temperature, \( \mu \) is the charge carrier mobility, \( A_e \) is the effective cross-sectional area (\( A_e = 1 \text{ cm}^2 \)), \( N_c \) is the density of the states available (\( N_c = 1.35 \times 10^{19} \text{ cm}^{-3} \)) [14], \( N_i \) is the density of traps, \( \phi_i \) is the energy level of the traps, \( V \) is the applied voltage, and \( d \) is the thickness of the \( \text{Fe}_2\text{O}_3 \) thin-films.

The trap concentration, \( N_i \), was estimated from the current-voltage characteristics, with the voltage which is related to slope change and that intersects to the potential drop, \( V_{\text{TFL}} \), across the films as indicated in both Figures 5 and 6 [25]. As shown in Figures 5 and 6, ohmic regime \( I \propto V \) was observed at low voltages (\( 0 < V < V_{\text{TFL}} \)), while at higher voltages (\( V_{\text{TFL}} < V < 5V \)), with \( I \propto V^n \) regime for \( n = 1.5 \) to 2. The parameter \( V_{\text{TFL}} \) corresponds to voltage associated with trap-filled limit with charge carriers and can be linked with the following relation:

\[ N_i = \frac{\varepsilon}{6e} \frac{V_{\text{TFL}}}{d^2}. \]

(2)

Nonlinear behavior on current-voltage characteristics was observed in Figures 5 and 6, which can be associated with collision-free transport at low voltages and collision-dominated transport at higher voltages [26]. It is known that collision-free transport associated with low-field transport is influenced by weak thermal vibrations and charge carrier mobility, \( \mu \), independent of the field because carriers and lattice are in equilibrium. However, under transport at higher voltages, the collision-dominated transport becomes a nonlinear function of carries with the field and charge carrier mobility, \( \mu \), into \( \text{Fe}_2\text{O}_3 \) thin-films [27].

Due to the fact that the charge carrier mobility in the space-charge-limited regime, \( \mu_{\text{SCL}} \), is connected to nonlinear-electronic transport of the samples, the value of \( \mu_{\text{SCL}} \) should be evaluated for the designing of adaptive electronic devices. \( \mu_{\text{SCL}} \) can be estimated from \( \Delta I = neA_e\Delta Vd^{-1} \) as

\[ \mu_{\text{SCL}} = \frac{d}{N_e A_e} m, \]

(3)

where \( m \) is first slope (ohmic region) on the current-voltage characteristics of Figures 5 and 6 and was extracted using \( m = \Delta I/\Delta V \), with \( \Delta I \) as the differential change of current and \( \Delta V \) as the differential change of voltage, respectively.

Table 1: Microstructure data for \( \text{Fe}_2\text{O}_3 \) thin-films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T ) (°C)</th>
<th>( d ) (nm)</th>
<th>( R_{eq} ) (nm)</th>
<th>( D ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>400</td>
<td>150</td>
<td>27.5</td>
<td>22.8</td>
</tr>
<tr>
<td>b</td>
<td>450</td>
<td>165</td>
<td>36.1</td>
<td>29.3</td>
</tr>
<tr>
<td>c</td>
<td>500</td>
<td>220</td>
<td>81.2</td>
<td>21.9</td>
</tr>
<tr>
<td>d</td>
<td>550</td>
<td>255</td>
<td>21.8</td>
<td>34.2</td>
</tr>
</tbody>
</table>
Fe$_2$O$_3$ Fe$_2$O$_3$ Fe$_2$O$_3$ Fe$_2$O$_3$ Fe$_2$O$_3$ Fe

$550^\circ C$

$500^\circ C$

$450^\circ C$

$400^\circ C$

$710^\circ C$

$200^\circ C$

$220$

$311$

$400$

$110$

$211$

$20$

$30$

$40$

$50$

$60$

$70$

$80$

$90$

$2\theta$ (deg)

Figure 4: XRD patterns of the oxidized samples under air atmosphere conditions.

Table 2: Transport parameters under forward bias.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{TFL}$ (V)</th>
<th>$N_t$ (cm$^{-3}$)</th>
<th>$m$</th>
<th>$\mu_{SCL}$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\alpha$</th>
<th>$\phi_t$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.2</td>
<td>$2.4 \times 10^{15}$</td>
<td>$6.5 \times 10^{-3}$</td>
<td>$0.26 \times 10^{-3}$</td>
<td>$1.5 \times 10^{-3}$</td>
<td>0.36</td>
</tr>
<tr>
<td>b</td>
<td>0.8</td>
<td>$1.3 \times 10^{15}$</td>
<td>$7.5 \times 10^{-3}$</td>
<td>$0.59 \times 10^{-3}$</td>
<td>$3.3 \times 10^{-3}$</td>
<td>0.37</td>
</tr>
<tr>
<td>c</td>
<td>1.1</td>
<td>$9.9 \times 10^{14}$</td>
<td>$5.7 \times 10^{-3}$</td>
<td>$0.78 \times 10^{-3}$</td>
<td>$2.7 \times 10^{-3}$</td>
<td>0.37</td>
</tr>
<tr>
<td>d</td>
<td>1.6</td>
<td>$1.1 \times 10^{15}$</td>
<td>$3.4 \times 10^{-3}$</td>
<td>$0.48 \times 10^{-3}$</td>
<td>$1.1 \times 10^{-3}$</td>
<td>0.36</td>
</tr>
</tbody>
</table>

It is assumed in (3) that $m$ can be extracted from ohmic region because low-field transport is used in characterizing semiconductor films to determine the concentration of thermally excited carriers, $n$, and its charge carrier mobility, $\mu$, [26]. Thus, under space-charge-limited regime, $N_t \gg n$ and (3) with $n = N_t$ was solved.

The space-charge-limited regime obeys to $I = \alpha V^n d^{-3}$, where $\alpha$ is a scaling factor which depends on $\varepsilon$, $\mu$, and $N_c / N_t$ ratio. According to (1), $\alpha$ is expressed by

$$\alpha = \frac{9}{32\pi}\varepsilon\mu A e \frac{N_c}{N_t} \exp \left( -\frac{\phi_t}{k_B T} \right).$$

(4)

Therefore, transport parameters of the Fe$_2$O$_3$ thin-films were extracted solving (2), (3), and (4) and using MATLAB program. Parameter $\alpha$ was estimated based on nonlinear behavior of Figures 5 and 6 and energy level of traps, $\phi_t$, was calculated from (4). Finally, transport parameters were listed for both forward and reverse bias in Tables 2 and 3, respectively.

From Tables 2 and 3, it was demonstrated that activation energy, $\phi_t$, for Fe$_2$O$_3$ layers varies nonmonotonically with temperature. The $V_{TFL}$ parameter was different for the samples, because slope changes were observed into the current-voltage characteristics, which is related to traps concentration changes, $N_t$, during the formation of discontinuous Fe$_2$O$_3$ thin-films. Contact effects of both Fe/Fe$_2$O$_3$ and Fe$_2$O$_3$/Cu interfaces may also influence device performance, because grain boundary scattering related with lattice defects-induced
trapping states near to the interface impedes the charge carrier motion by space-charge phenomena.

Nonlinear-electronic transport in samples with lower critical thickness of 250 nm varies monotonically with the low charge carrier mobility, $\mu_{SCL}$, in the space-charge-limited regime [8, 25]. The low charge carrier mobility in Tables 2 and 3 was affected by bias because the $\text{Fe}_2\text{O}_3$ phase provides strong cohesive forces with iron foil and allows a carriers transport with increase of $\mu_{SCL}$ under forward bias. However, because structural defects are formed into $\text{Fe}_2\text{O}_3$ thin-films

Table 3: Transport parameters under reverse bias.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{TFL}$ (V)</th>
<th>$N_e$ (cm$^{-3}$)</th>
<th>$m$</th>
<th>$\mu_{SCL}$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\alpha$</th>
<th>$\phi_i$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.8</td>
<td>$1.5 \times 10^{15}$</td>
<td>$2.5 \times 10^{-3}$</td>
<td>$0.15 \times 10^{-3}$</td>
<td>$3.0 \times 10^{-3}$</td>
<td>0.34</td>
</tr>
<tr>
<td>b</td>
<td>1.6</td>
<td>$2.7 \times 10^{15}$</td>
<td>$3.0 \times 10^{-3}$</td>
<td>$0.11 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>0.34</td>
</tr>
<tr>
<td>c</td>
<td>1.8</td>
<td>$1.6 \times 10^{15}$</td>
<td>$3.1 \times 10^{-3}$</td>
<td>$0.26 \times 10^{-3}$</td>
<td>$9.6 \times 10^{-3}$</td>
<td>0.35</td>
</tr>
<tr>
<td>d</td>
<td>1.1</td>
<td>$7.7 \times 10^{14}$</td>
<td>$3.7 \times 10^{-3}$</td>
<td>$0.77 \times 10^{-3}$</td>
<td>$2.8 \times 10^{-3}$</td>
<td>0.36</td>
</tr>
</tbody>
</table>
during the oxidation process, weak cohesive forces between Fe$_2$O$_3$ phase and copper contact allow a carriers transport with decrease of $\mu_{SCL}$ under reverse bias. Finally, increase of average roughness, $R_{avg}$, and smaller crystalline size, $D$, in correlation with changes of charge carrier mobility, $\mu_{SCL}$, is a consequence of space-charge-limited transport in Fe$_2$O$_3$ thin-films.

4. Conclusion

Nonlinear-electronic transport from Fe$_2$O$_3$ thin-films was studied by current-voltage characteristics as a function of the oxidation temperature. Both average roughness and grain size were demonstrated by atomic force microscopy and X-ray diffraction studies. Transport parameters were evaluated for all samples at room temperature. Space-charge effects were related to the formation of discontinuous oxide based on discontinuous grain growth during the oxidation process at intermediate temperatures. Analysis of current-voltage characteristics shows ohmic regime at low voltages and space-charge-limited regime at higher voltages.

Further, the iron oxide samples with lower critical thickness of 250 nm can be useful for the designing of adaptive oxide electronic devices, because the current flow in the Fe$_2$O$_3$ thin-films with low carrier mobility and low energy level of the traps, can be gradually modulated.
Conflict of Interests
The author declares that there is no conflict of interests, such as financial gain, but there is a direct interest regarding the publication of this paper to share knowledge in this area.

Acknowledgments
The process and results obtained in this work have been possible thanks to the previous support of Dr. Ramón Peña Sierra from CINVESTAV-IPN and Dr. Juan Vicente Méndez Méndez from CNMN-IPN, Mexico.

References