Influence of Iron Nanowires Oxidation on Their Semiconducting Properties

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The main aim of this work was to study the impact of thermal annealing on the structure of iron oxide shell covering iron nanowires in relation to their semiconducting properties. Studied nanomaterial has been produced via a simple chemical reduction in an external magnetic field and then it has been thermally-treated at $400\,°C$, $600\,°C$ and also $800\,°C$ in a slightly oxidizing argon atmosphere. Annealed iron nanowires have been characterized by means of the Raman spectroscopy and photoluminescence in order to study the structure of iron oxide shell and its influence on semiconducting properties of the whole nanostructure. According to obtained experimental results, the composition of iron oxide shell covering the studied nanomaterial is changing with annealing temperature. The thermal treatment at $400\,°C$ leads to oxidation of iron coming from the core of nanomaterial and formation of a mixture of Fe_3O_4 and α-Fe_2O_3 on the surfaces of nanowires, while annealing at higher temperatures results in further oxidation of iron as well as the phase transformation of previously created Fe_3O_4 into the most thermodynamically stable form of iron oxide at ambient conditions — α-Fe_2O_3. This oxide has a major impact on the semiconducting properties of studied nanomaterial. Thereby, the measurements of photoluminescence enabled to estimate the bandgap of bulk and surface layer at about 1.8 eV and 2.1 eV, respectively.

1. Introduction

Recently, the metal oxide nanomaterials have become a source of advanced studies ranging from semiconductors to insulators. These materials are very attractive because their properties can be easily-tuned by changing their stoichiometry, coordination, size, shape as well as dimensionality [1]. Among all of metal oxide nanomaterials, the iron oxide nanostructures seem to be interesting due to their unique chemical, magnetic and also electrical properties. The thermodynamically stable iron oxides at ambient conditions can be treated as either the conductors (e.g. Fe_3O_4) or the semiconductors (e.g. γ-Fe_2O_3, α-Fe_2O_3) [1, 2]. This fact should be taken into account during a preparation of iron-based nanomaterials for different applications.

The growth of oxide by a thermal oxidation of metals is quite simple process. Hence, it is commonly applied in the large-scale fabrication of different metal oxide nanostructures [1, 3–5]. Following this trend, similar operation has been performed for iron nanowires (Fe NWs) produced via a simple chemical reduction in an external magnetic field [6]. Naturally, such thermal treatment affects the properties of studied nanowires. In the previous reports, there were presented how the thermal oxidation in a slightly oxidizing argon atmosphere influenced on the structure and the magnetic properties of iron nanowires [7–9]. Referring to these publications, further studies have been carried out in order to study the

impact of changing iron oxide shell structure covering Fe NWs caused by the thermal annealing in relation to the semiconducting properties of this nanomaterial.

2. Experimental part

Iron nanowires were produced as a result of simple reduction reaction of 0.2 mL 0.5 M hexahydrated iron (III) chloride ($FeCl_3 \times 6H_2O$; 98%, Sigma-Aldrich) with 2 mL 1 M sodium borohydride ($NaBH_4$; 98%, Sigma-Aldrich). Moreover, the reaction was carried out in a constant argon flow as an inert gas and with an application of external magnetic field of about 0.2 T (2000 G). Obtained iron nanowires were washed several times with ethanol (99.5%, Shimakyu's Pure Chemicals Company) and then they were dried in a vacuum oven at $80\,°C$. The details for the fabrication process of studied nanomaterial can be found in Ref. [6]. After that, iron nanowires were subjected to a thermal treatment in a tube furnace with a constant argon flow containing a trace amount of oxygen. Annealing was performed for 30 min at $400\,°C$ (Fe NWs $400\,°C$), at $600\,°C$ (Fe NWs $600\,°C$) and at $800\,°C$ (Fe NWs $800\,°C$).

The properties of as-prepared and annealed iron nanowires were characterized at room temperature by: a Bruker D2 Phaser diffractometer (XRD) equipped with a Cu sealed tube (X-ray source; $\lambda = 0.1542$ nm) and a LYNXEYE detector, and a T64000 Series II spectrometer equipped with a continuous wave 532 nm (2.33 eV) Nd-YAG laser and a multichannel high-resolution Si-CCD camera.

3. Results and discussion

It is commonly known that the most thermodynamically stable form of iron oxide at ambient conditions is

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hematite (α-Fe$_2$O$_3$) which can be treated as a semiconductor with the bandgap typically observed between 2.1 and 2.2 eV [10]. Therefore, the gradual oxidation of studied nanowires into α-Fe$_2$O$_3$ has a main impact on their semiconducting properties.

According to X-ray diffraction (XRD) patterns presented in Fig. 1, as-prepared iron nanowires are composed of α-Fe crystalline phase, while the progressive thermal treatment up to 800 °C in the argon atmosphere results in formation of crystalline corundum-type α-Fe$_2$O$_3$. No signals originating from iron oxides and iron can be observed for spectra of Fe NWs and Fe NWs heated at 800 °C, respectively. However, the previous studies of iron nanowires [7–9] show that as-prepared nanomaterial is covered by a very thin oxide layer while Fe NWs annealed at 800 °C contain a low amount of iron. The oxide shell of initial wire-like nanostructure can be considered as Fe$_3$O$_4$ whose bandgap is around 0.14 eV [2]. Therefore, iron and Fe$_3$O$_4$ phase do not have a significant effect on the semiconducting properties but they should result in a good conduction of material.
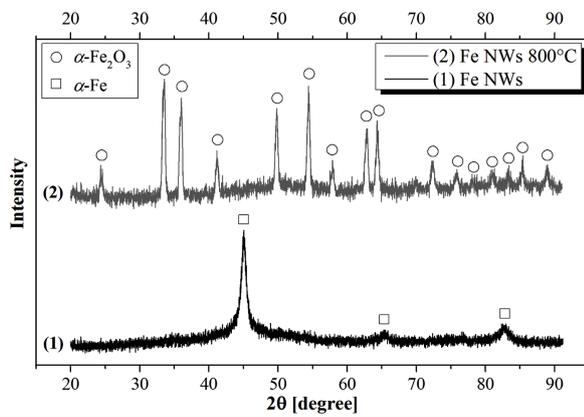
Fig. 1. XRD patterns of (1) as-prepared iron nanowires and (2) iron nanowires annealed at 800 °C. Positions of peaks determined according to JCPDS cards with numbers 87-0722 (α-Fe) and 84-0311 (α-Fe$_2$O$_3$).

The evolution of the iron oxide shell structure of nanowires observed by the Raman spectroscopy is shown in Fig. 2. Analyzing the spectra, one can see that the thermal treatment at 400 °C leads to oxidation of iron coming from the core of studied nanomaterial and formation of a mixture of Fe$_3$O$_4$ and α-Fe$_2$O$_3$ on the surfaces of nanowires, while annealing at higher temperatures results in further oxidation of iron as well as the phase transformation of previously created Fe$_3$O$_4$ into hematite. As-prepared nanowires seem to be covered by a thin amorphous or highly-defected oxide layer which cannot be detected by this technique. Observed Raman vibrational modes correspond well to positions of iron oxides bands reported in Ref. [11].

The photoluminescence (PL) spectra of as-prepared as well as annealed iron nanowires are shown in Fig. 3. All of them have been recorded with the excitation wave-
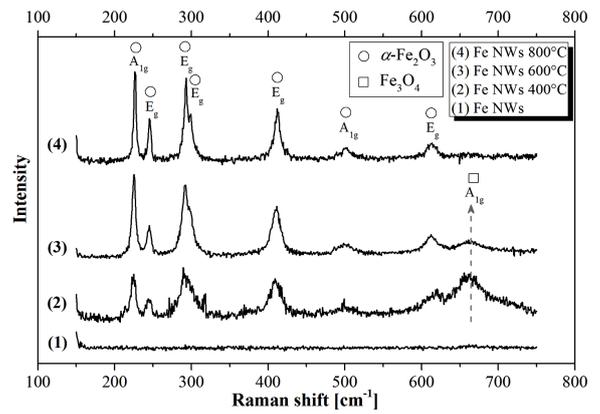
Fig. 2. Raman spectra of (1) as-prepared iron nanowires and Fe NWs annealed at (2) 400 °C, (3) 600 °C, and (4) 800 °C.
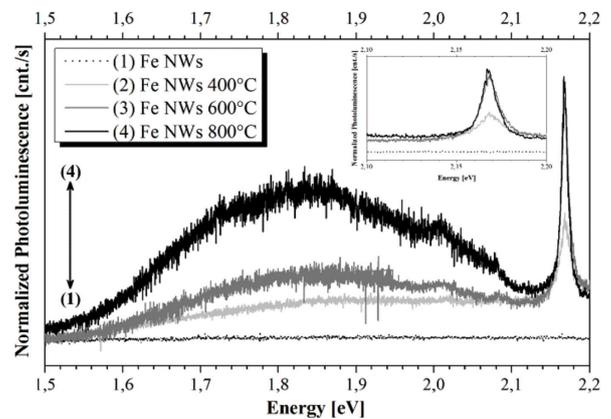
Fig. 3. Photoluminescence spectra registered for (1) as-prepared Fe NWs; (2) Fe NWs annealed at 400 °C; (3) Fe NWs annealed at 600 °C and (4) Fe NWs annealed at 800 °C. Inset: more detailed view on the PL spectra in the range from 2.1 eV to 2.2 eV. All spectra recorded for laser excitation of 532 nm.

length of 532 nm. Besides the spectrum of as-prepared nanowires, all the PL spectra consist of two bands. In the case of initially formed nanowires, this result is in good agreement with the structural properties discussed above. The as-prepared Fe NWs do not contain in their structure any iron oxides which could influence on their semiconducting properties. In turn, the presence of two bands in the PL spectra is associated with the existence of α-Fe$_2$O$_3$ in the studied nanomaterial. In the case of thermally-treated samples, one of PL band is very broad with quite low intensity and maximum depending on the temperature in which nanowires have been annealed. The energy position of maximum changes from 1.92 eV (646 nm), 1.88 eV (660 nm) to 1.84 eV (674 nm) for Fe NWs 400 °C, Fe NWs 600 °C, and Fe NWs 800 °C, respectively. These values are comparable to those found in the literature for α-Fe$_2$O$_3$ nanowires [1] and array of α-Fe$_2$O$_3$ nanorods [12]. The redshift of this band

may be related to an increase of nanowires size [13]. In contrast to the first band, the maximum of the second one is permanent for all spectra and it is centered at 2.16 eV (574 nm), which is consistent with the value of bulk α-Fe_2O_3 [10]. Moreover, this peak is sharp, narrow and its intensity is higher than intensity of former band. Similar observation has been reported for α-Fe_2O_3 nanowires [14]. The presence of two bands in PL spectra may be attributed to different values of bandgap for surface layer and bulk of α-Fe_2O_3. This can be explained considering that the intensities of both PL peaks enhance with increasing annealing temperature of Fe NWs. Firstly, the initial oxidation of iron nanowires leads to formation of a thin α-Fe_2O_3 layer which is placed mainly on their surfaces. The gradual increase of temperature results in more and more oxidation of studied nanomaterial which causes the enhancement of the signal coming from the bulk.

4. Conclusions

The results presented in this work show that the presence of the α-Fe_2O_3 has the major impact on the semiconducting properties of studied iron nanowires. The progressive oxidation of investigated nanomaterial leads to formation of a thin hematite layer, which is initially placed on their surfaces. Next stages of thermal treatment result in further oxidation of iron coming from the core of Fe NWs and the phase transformation of previously created Fe_3O_4 into α-Fe_2O_3. This causes that two bands of PL can be detected and assigned to different values of bandgap for bulk and surface layer which have been estimated as about 1.8 eV and 2.1 eV, respectively. Therefore, the size and shape of nanomaterial also play an important role, which has the strong impact on the signal of photoluminescence.

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