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A novel method for metal oxide nanowire synthesis

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Abstract
Nanowires (NWs) of metal oxides (Fe$_2$O$_3$, CuO, V$_2$O$_5$ and ZnO) were grown by an efficient non-catalytic economically favorable method based on resistive heating of pure metal wires or foils at ambient conditions. The growth rate of iron oxide NWs exceeds 100 nm s$^{-1}$. Produced NWs were typically 1–5 μm long with diameters from 10 to 50 nm. The produced metal oxide NWs were characterized by means of SEM, TEM, EDX, XPS and Raman techniques. The field emission measurements from the as-produced CuO NWs were found to have a threshold field as low as 4 V μm$^{-1}$ at 0.01 mA cm$^{-2}$. The formation mechanism of the NWs is discussed.

Supplementary data are available from stacks.iop.org/Nano/20/165603

1. Introduction

After Iijima's landmark publication [1], carbon nanotubes and soon after other quasi-one-dimensional materials such as non-carbon nanotubes, nanowires and nanorods attracted a tremendous interest in the scientific community [2–5]. Semiconductor NWs offer reproducible properties, which do not depend on the size as compared to carbon nanotubes, but are inherited from their bulk form. Among different quasi-one-dimensional materials, metal oxide NWs are very interesting for diverse applications, such as chemical and biosensors [6, 7], solar cells [8], field emission devices [9], other electronic and optoelectronic devices [10] etc. Metal oxide NWs have been successfully synthesized by various methods. The methods based on thermal metal evaporation [11], chemical vapor deposition (CVD) [12–14] and plasma enhanced chemical vapor deposition (PECVD) [15] reported to date require long synthesis time, high energy consumption, catalyst use or high temperatures; consequently, the economical efficiency of oxide NW synthesis is limited. Hydrothermal synthesis [16, 17] can be applied at low temperatures, although the time required for the synthesis is from hours to days. Direct furnace thermal oxidation below the metal melting point in air [18] oxygen [19] or other gases [20] is interesting for its simplicity, although production process times are from hours to days. The reactive oxygen plasma method [21] offers rapid synthesis, but application of complicated equipment is a cost effectiveness issue.

In this paper, we propose a very simple non-catalytic one-step process method for an efficient and rapid synthesis of NWs by direct resistive heating of metals. This method does not necessarily require a controlled atmosphere, since the synthesis can be carried out in ambient conditions; the process of NW formation is very rapid, with a typical growth...
time of a few seconds, and consuming very little energy compared to traditional methods. The simplicity of the method and possibility to rapidly heat up the substrate allowed us to investigate and discuss the mechanism of the NW formation from different metals. An application of the as-produced NWs for cold electron emitters is shown.

2. Experimental method

2.1. Materials and synthesis conditions

As substrates, metal wires 0.25 mm in diameter or foils with 0.1–0.04 mm thickness were used. For our studies we used Mo (99.97%), Cu (99.99%), W (99.9% +%) and Ti (99.6% +%) wires purchased from Aldrich Chemical, and Co, Zn (both 99.99% +%), Fe (99.99% and 99.5%), V (99.8%), Ni (99.98%), Pd (99.9%), Sn (99.99% +%) and In (99.999%) wires purchased from Goodfellow Cambridge Ltd. Ambient air conditions corresponded to regular laboratory and atmospheric pressure conditions with a temperature from 21 to 24 °C and a relative humidity from 20 to 45%.

The synthesis of NWs was carried out in ambient laboratory conditions by means of a simple resistive heating of as-received pure metal wires or foils suspended between two electric contacts (supporting information, figure S1 available at stacks.iop.org/Nano/20/165603). The samples were heated by direct current using a standard laboratory power supply. For heating the substrates to synthesis temperatures, an electric current from 1 to 9 A (corresponding to a power of 2–8 W) depending on the material was required. The wire temperature during the growth was monitored by an IR pyrometer (Infratherm IGA 12-s) with a 0.1 mm spot size. The NW synthesis duration was varied from 2 s to 3 min.

2.2. Characterization and measurements

Electron microscopic studies were performed with a Leo 982 Gemini scanning electron microscope (SEM) and a Philips CM200 FEG transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) was carried out with a Surface Science Instruments SSX-100 ESCA spectrometer using monochromatic Al Kα x-rays (1486.6 eV). Core-level spectra were recorded with a pass energy of 60 eV and an x-ray spot size of 300 μm. The binding energy scale was referenced to the characteristic carbon 1s binding energy of 285 eV. Raman spectra were obtained with a Wintech alpha300 spectrometer using a frequency doubled Nd:YAG green laser (λ = 532 nm). In order to minimize possible sample degradation, low laser power of about 160 μW was used for the measurements.

For field emission (FE) property measurements the samples were placed in a vacuum diode field emission set-up and used as cathodes. FE current–voltage characteristics were obtained by applying a pulsed voltage between electrodes up to 10 kV with pulse duration of about 15 μs and with a repetition frequency of 200 Hz. The middle parts of the foils or wires 1 cm long were mounted on the steel substrates parallel to a flat anode. To characterize the spatial distribution of the emission sites over the sample surface a conductive cathodoluminescent screen was used as the anode. The distance between electrodes was varied from 100 to 500 μm with a high precision screw translator.

3. Results

In order to demonstrate the simplicity and rapidness of our method we selected four metals: Fe, Cu, V and Zn (figure 1). Nevertheless, our preliminary investigations showed that promising results could be also obtained with other metals, such as W, Al and Mo, as shown in supporting information figure S2 (available at stacks.iop.org/Nano/20/165603). However, our trial experiments with Ni, Pd, Sn, In and Ti wires did not result in the growth of NWs.

The successful NW synthesis was carried out in the range of 400–700 °C, i.e. at temperatures below the melting temperature of the used metals, except Zn. A resistive heating of the wires and foils provides uniform temperature distribution in their middle parts. SEM and TEM observations revealed that the middle part of the wire (foil) surfaces is evenly covered by NWs. The areas in the vicinity of contacts had lower temperature due to the heat losses and thereby did not contain NWs. It is worth noting that higher coverage with NWs can be obtained by using longer wires (figure S1c, available at stacks.iop.org/Nano/20/165603).

SEM and TEM observations showed that produced NWs were preferentially orientated perpendicularly to the substrate surface. Electron diffraction experiments have been carried out to investigate the structures of the NWs with electron diffraction patterns (EDPs) shown in figure 1. These EDPs have been indexed as orthorhombic Fe2O3 (a = 0.503 nm, c = 1.375 nm), monoclinic CuO (a = 0.469 nm, b = 0.342 nm, c = 0.513 nm), orthorhombic V2O5 (a = 1.154 nm, b = 0.438 nm, c = 0.357 nm) and hexagonal ZnO (a = 0.325 nm, c = 0.521 nm). In the case of Fe wire-, blade- and rod-like Fe2O3 NWs were synthesized (figure 1). The NWs were from 1 to 5 μm long with the highest density on the substrate surface at the synthesis temperatures from 690 to 720 °C. CuO NWs with the highest density on Cu foils and wires were formed in the temperature range of 420–480 °C. The CuO NWs had rod shapes with the diameter from 20 to 50 nm and with the length from 0.5 to 2 μm. Resistive heating of V wires and foils at ambient conditions in the temperature range of 450–480 °C resulted in the highest density of V2O5 NWs. V2O5 NWs had rod-like structures with the diameters of 50–60 nm and lengths of 0.5–1 μm. Oxidation of Zn wire led to the formation of ZnO NWs in a wide temperature range from 500 to 700 °C with a diverse morphology. At lower temperatures (500–600 °C) mainly rod-like and belt-like NWs with diameters of 8–20 nm and lengths of 1–10 μm were observed; some NWs are branched. Increasing the synthesis temperature to about 700 °C resulted in the formation of NWs of 1–5 μm in length with blade shapes. From SEM images the highest density of surface coverage was observed for Fe2O3 and ZnO NWs and lower for CuO and V2O5 NWs.

The chemical composition of the substrate wires after the synthesis was evaluated by Raman spectroscopy measurements (figure 2). The spectrum obtained from iron oxide NWs is...
Figure 1. The results of electron microscopy investigations of Fe$_2$O$_3$, CuO, V$_2$O$_5$ and ZnO NWs. Columns from left to right respectively show SEM images of NWs, low and intermediate magnification TEM images of NWs and electron diffraction patterns (EDPs) with indices determined by their crystal structure.

shown in figure 2(a). Peaks located at 225, 245, 292, 411, 498, 611 and 1323 cm$^{-1}$ correspond to $\alpha$-Fe$_2$O$_3$. The presence of small amount of Fe$_3$O$_4$ can also be detected as a peak at 663 cm$^{-1}$ [22, 23]. The Raman modes originating from CuO and Cu$_2$O are both observed in the spectrum measured from Cu wire (figure 2(b)). The peaks at about 298, 342 and 633 cm$^{-1}$ correspond to the $A_g$, $B_{1g}$ and $B_{2g}$ modes of CuO, respectively [24, 25]. The peaks at 219, 342 and 411 can be assigned to Cu$_2$O. There is also a contribution of Cu$_2$O to the band centered at around 633 cm$^{-1}$, which makes this peak broader and more intensive than pure CuO [26–29]. The little shift of Raman frequency and profile broadening could be caused by the nanocrystalline structure [30]. The Raman spectrum of NWs grown on V wire shows two kinds of vanadium oxides with oxidation state of +5 and +4 (figure 2(c)). Peaks at about 146, 194, 281, 309, 479, 525, 699, 994 and 403 cm$^{-1}$ visible as a shoulder can be indexed as V$_2$O$_5$ structure [31–33]. Raman modes from VO$_2$ can also be seen at 222, 339, 392, 446, 498 and 614 cm$^{-1}$. The peaks at 194 and 309 cm$^{-1}$ are contributed from both V$_2$O$_5$ and VO$_2$; consequently, they are more intense [34, 35]. Raman spectra of zinc oxide NWs (figure 2(d)) reveal the peak centered at 438 cm$^{-1}$, which corresponds to the E2 mode of ZnO [36]. The Raman scattering peak at 561 cm$^{-1}$ is related to the oxygen deficiency in ZnO [37].

The chemical composition of the surface layer with NWs was confirmed by means of the XPS technique. The chemical state of Fe wire can be determined from the Fe 2p spectrum shown in figure 3(a). The Fe 2P$_{3/2}$ maximum was found at approximately 710 eV and the satellite peak between the 2P$_{3/2}$
and $2p_{1/2}$ peaks around 719 eV [38]. The positions of these peaks as well as the shape of the Fe 2p spectrum agree well with Fe$^{3+}$ state characterization reported by Aronniemi et al [39]. The Cu 2p spectrum for copper oxide NWs is shown in figure 3(b). The observed $2p_{3/2}$ binding energy corresponds to CuO. The multiple peaks observed are typical for the CuO phase and can be interpreted as metal–ligand charge transfer satellites [38, 40]. XPS spectra of vanadium oxide nanorods (figure 3(c)) show a mixture of different oxidation states, mainly V$^{5+}$ and V$^{4+}$, but also small amounts of V$^{3+}$ could be present. An analysis of the V 2p spectrum [41] revealed that the atomic concentrations of V$^{5+}$ and V$^{4+}$ of all vanadium were about 85% and 15%, respectively. Figure 2(d) shows the Zn 2p region and the LMM Auger region measured to characterize zinc oxide. The Auger parameter was utilized for the characterization, since the Zn and ZnO 2p binding energy values are very close. The Auger parameter was calculated as the sum of the Zn $2p_{3/2}$ binding energy and the Auger $L_3M_{45}M_{45}$ kinetic energy to be 2010.2 eV, which is typical for ZnO [40]. The calculated atomic ratio of Zn and O also supports the oxidation of Zn wire to ZnO.

From TEM, Raman and XPS measurements it can be concluded that metal wires are covered by NWs of the corresponding metal oxide. NWs were indexed by EDP as Fe$_2$O$_3$, CuO, V$_2$O$_5$ and ZnO. Peaks from several oxides appear in the Raman spectra; however, XPS shows only one metal oxide (except for vanadium): Fe$_2$O$_3$, CuO and ZnO. This can be explained by the different depth resolutions of these two methods. The Raman depth resolution is in the range of a micron, whereas the XPS signal comes from only a few topmost atomic layers. Nevertheless, the presence of small amounts of lower oxidation state metal oxides on the surface cannot be excluded, as the sensitivity limit of XPS is about 1%.

For investigations of NW growth kinetics, we applied a potential difference to wires (to heat them up to the optimum temperature) for a certain period of time. After this time the wires were rapidly cooled down by switching the power off. In the case of Fe, already after 2–4 s, $\alpha$-Fe$_2$O$_3$ NWs with a length of about 200 nm were found on the surface of the treated wires (figure 4(a)). It can be estimated that the growth of $\alpha$-Fe$_2$O$_3$ NWs is very rapid and the growth rate exceeds 100 nm s$^{-1}$. A dense NW ‘forest’ was produced after 40 s and no changes were observed after longer heat treatment time. Similar investigations carried out with Zn, V and Cu revealed the presence of NWs already after 10 s treatment time.
Figure 3. XPS spectra obtained from different metal oxide NWs: (a) Fe 2p region of iron oxide sample; (b) Cu 2p region of copper oxide sample; (c) V 2p and O 1s region of vanadium oxide sample with fitting; (d) Zn 2p region of zinc oxide sample.

Needle-like nanoscale arrays are expected to possess low voltage field electron emission properties due to the electric field enhancement effect on the nanostructured tips [42]. For the FE property examination, the samples were used without any pretreatment as cathodes in a vacuum diode field emission set-up. In order to compare the results obtained for different samples the current–voltage ($I$–$V$) curves were converted to current density dependences on electric field ($J$–$E$). The distance between cathode and anode was controlled by using a precision screw translator. The electric field intensity, $E$, in the diode was defined as a ratio of applied voltage, $V$, to the inter-electrode distance. The current density, $J$, was defined as a ratio of cathode current, $I$, to the emitting cathode area estimated from the emission pattern on the luminescent screen. The obtained FE patterns for wires and foils were quite homogeneous for all types of metal oxide samples (figure 5(a)). $J$–$E$ dependences of samples with NWs are presented in figure 5(b). The approximation of $J$–$E$ curves with the Fowler–Nordheim equation gives a good agreement with the tunneling mechanism of emission [43].

V$_2$O$_5$, ZnO and Fe$_2$O$_3$ NWs have higher threshold fields and lower maximum current densities, as can be seen in figure 5 and table S1 (supporting information available at stacks.iop.org/Nano/20/165603). The samples with CuO NWs showed the best FE characteristics. The threshold field value corresponding to the current density of 0.01 mA cm$^{-2}$ was about 4 V $\mu$m$^{-1}$. The maximum current density for samples with CuO NWs was about 100 mA cm$^{-2}$. These parameters are comparable with the best FE characteristics reported for different metal oxide structures produced by other methods [44–47].

4. Discussion

In this work, a non-catalytic method for the rapid growth of metal oxide NWs by an oxidation at ambient conditions is demonstrated. This method is very simple and does not require any expensive and complicated equipment. In the simplest approach, the NWs could be grown in ambient conditions using a car accumulator or a set of household batteries. The NW growth requires 2–8 W of energy for a 3 cm long sample, which is a thousand times less than the energy consumed during conventional synthesis methods. Usually the growth
of a dense NW forest takes a few hours [11, 16–20], while in our case 40 s was enough to completely cover the surface of the substrate. The growth rate of the iron oxide NWs exceeded 100 nm s$^{-1}$, which is to the best of our knowledge the highest rate so far reported. This high growth rate can be explained by the temperature profile across the wire and the
high heating rate: in our method the wire is heated from inside and very quickly, providing a higher temperature gradient across the wire compared to the conventional furnace oxidation techniques. Thus, the resistive heating method for the growth of NWs is the most simple and rapid one.

Even though the same method was used to synthesize NWs from Fe, Cu, V and Zn metals, the mechanisms of their growth may differ. Equilibrium vapor pressures of the metals at the synthesis temperatures are quite low, except for Zn (supporting information figure S3, available at stacks.iop.org/Nano/20/165603). Therefore, the formation of NWs on the surface of Fe, V and Cu from the vapor phase can be excluded and should be discussed separately from mechanism of ZnO NW growth.

Typically, the NW growth during oxidation of metal has been explained by the stress driven mechanism [48–51], in which a relaxation of the large stresses results in the NW formation generated by dislocation slips. Substantial stresses are expected to be accumulated on the interface due to their structural and density differences [51]. It is believed that in the stress driven mechanism the metal oxide layer provides a path to release the stress in the form of NWs. However, this mechanism fails to explain the existence of the growth temperature window. Also, the formation of single crystal structures by a simple extrusion is a very unlikely process. Another argument against the stress driven mechanism is a simple estimation of densities of different oxide layers which are formed during the process of NW formation. It is well known that metals form different oxide layers: an iron wire from the inside to the surface is covered by FeO, Fe2O3 and Fe3O4 [52]; copper is covered by Cu2O and then by CuO on the surface [53] (supporting information figure S4, available at stacks.iop.org/Nano/20/165603). Simple density estimations of different oxide layers (molecular volume increase with respect to the underlying layer) show that the volume increase in the FeO layer is 77% with respect to Fe, Fe2O3 has an increase as large as 255% with respect to FeO, while the formation of Fe3O4 is accompanied by a 32% decrease in the molecular volume. This means that the stress must be mainly accumulated in Fe2O3 and FeO layers and can not directly affect the growth of NWs. In the case of copper, the stress can also be accumulated in the Cu2O layer as the molecular volume increase is 236%, followed by a 47% decrease in the CuO layer.

We believe that the growth of NWs is determined by diffusion processes. The driving force for the motion of metal and oxygen ion species is the potential difference appearing during the wire oxidation process. The electric field strength between metal and oxide layers is very high, e.g. in the case of iron oxidation it is 10^6 V cm^{-1} [52]. It is worth noting that in order to resistively heat the wire the electric field strength is six orders of magnitude lower and thereby can not significantly affect the ion motion. The metal oxidation process involves metal ion diffusion from the wire core to the surface through the metal oxide layers and oxygen ions in the opposite direction [52, 53]. At elevated temperatures, the grain boundary diffusion rate is significantly higher compared to the lattice diffusion [54]. In the initial stage, the surface metal oxide phase might grow in all directions; however, only such a crystallographic direction endures which follows energetically favorable conditions [49], such as easier diffusion and advantageous stacking. During the NW growth, metal ions coming from the bottom to the top are diffusing through defects in NWs or by surface diffusion. It is worth noting that the NW cone-like shape confirms that the growth is determined by the diffusion process from the bottom, where the NWs are thicker, to the top, where they become thinner.

The described mechanism can partially explain the growth of ZnO NWs, even though the equilibrium Zn vapor pressure is significant at the growth temperatures. The growth mechanism of ZnO NWs can be presented as a formation of a protective ZnO layer (supporting information figure S4 available at stacks.iop.org/Nano/20/165603), which preserves the shape of the wire above the Zn melting point (420 °C) and Zn evaporation. Most likely both mechanisms of Zn vapor penetration through the protective ZnO layer to the outer shell and diffusion of Zn species through the ZnO layer can happen. Indeed, ZnO NWs are similar to Fe2O3, CuO and V2O5 ones; however, they contain dendrite structures (seen in the TEM image of figure 1), confirming the occurrence of the vapor growth mechanism.

FE measurements of the produced NWs revealed enhanced electron emissive properties of the NWs, especially for CuO. A significant difference in the FE properties, which can not be explained based on macroscopic properties of the metal oxides, was also observed. The work function of the oxide materials varies from 5 to 6 eV. This difference in work function value is not enough to explain the variation in the FE behavior. Therefore, the FE property alteration should be explained by the NW morphology, i.e. by the shape of individual NWs and their spatial density. The different metal oxide NWs observed in SEM and TEM have very similar quasi-one-dimensional shape (either rod or needle-like structures), therefore the enhancement factor and the field penetration effect for individual NWs should be similar. The main difference in the morphology, which can explain the difference in the FE efficiency, appears to be the spatial density of NWs on the surface. It is interesting to note that ZnO and Fe2O3 NWs, which were synthesized with the highest NW density, showed the worst FE properties. In contrast, V2O5 and CuO NWs demonstrating the highest FE efficiency were less uniform and had smaller NW density. As has been recently reported [42], the highest current density corresponds to the optimum distance between emitters, which is a double emitter height. In other words, for the best electron emitting properties the distance between NWs should be twice their length. Therefore, in the case of ZnO and Fe2O3 NWs, the field enhancement factor for each emitter (NW) was significantly reduced due to the screening effect [42]. The difference in the emission site densities of different materials can be clearly seen in the FE patterns (figure 5). Thus, the FE properties of the metal oxide NW samples are mainly determined by the spatial density of the NWs on the sample surface. It is worth noting that the observed efficient FE from examined metal oxide NWs is very promising for applications in vacuum electronic devices.
5. Conclusion

We proposed a very simple, rapid and inexpensive method for metal oxide NW growth based on resistive heating of metals at ambient conditions. As a result, Fe$_2$O$_3$, CuO, V$_2$O$_5$ and ZnO NWs were synthesized and thoroughly characterized. The possibility of growth of metal oxide NWs was also demonstrated with Al, W and Mo. Fe$_2$O$_3$ NW formation was detected already after 2 s of heating; other metal oxide NWs were grown after 10 s. The $\alpha$-Fe$_2$O$_3$ NW growth rate was found to exceed 100 nm s$^{-1}$. The mechanism of the NW growth is based on the faster diffusion of metal ions to the surface of the wire through grain boundaries and to the tip of the growing NW through defect diffusion and by surface diffusion. In the case of ZnO NWs, vapor phase growth plays an important role.

The observed FE properties showed very promising results for applications of the metal oxide NWs in vacuum electronic devices. Cold electron FE measurements showed that CuO NWs possess excellent FE properties with a very low threshold field of 4 V $\mu$m$^{-1}$ at 0.01 mA cm$^{-2}$. The reduction in the FE efficiency for the different metal oxide NWs produced by our method was explained by the increase in the NW spatial density on the sample surface and, thereby, by the increase in the screening effect.

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