

Stable field emission from arrays of vertically aligned free-standing metallic nanowires

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Abstract

We present a fully elaborated process to grow arrays of metallic nanowires with controlled geometry and density, based on electrochemical filling of nanopores in track-etched templates. Nanowire growth is performed at room temperature, atmospheric pressure and is compatible with low cost fabrication and large surfaces. This technique offers an excellent control of the orientation, shape and nanowires density. It is applied to fabricate field emission arrays with a good control of the emission site density. We have prepared Co, Ni, Cu and Rh nanowires with a height of 3 μm , a diameter of 80 nm and a density of $\sim 10^7 \text{ cm}^{-2}$. The electron field emission measurements and total energy distributions show that the as-grown nanowires exhibit a complex behaviour, first with emission activation under high field, followed by unstable emission. A model taking into account the effect of an oxide layer covering the nanowire surface is developed to explain this particular field emission behaviour. Finally, we present an *in situ* cleaning procedure by ion bombardment that collectively removes this oxide layer, leading to a stable and reproducible emission behaviour. After treatment, the emission current density is $\sim 1 \text{ mA cm}^{-2}$ for a 30 V μm^{-1} applied electric field.

1. Introduction

Field emission (FE) from one-dimensional systems such as nanowires (NWs) and carbon nanotubes (CNTs) has been extensively studied over the last decade for both a fundamental understanding and for numerous potential applications. These include field emission displays (FEDs) [1, 2], backlight units for liquid crystal displays [3] and other field emission devices

such as microwave amplifiers [4] and electronic sources for scientific instrumentation [5].

As far as field emission displays are concerned, different approaches for CNT integration have been studied. While the Samsung Lab [6] used post-growth CNT deposition, Dijon *et al* [7] fabricated devices with CNT growth performed directly inside a triode structure. Both of these CNT-based technologies have certain drawbacks. The Samsung approach is based on the deposition (by screen printing) of a CNT paste containing an

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epoxy resist, which induces problems of electrical connection between the carbon nanotubes and the substrate (cathode). Due to the poor carbon nanotube/substrate contacts, good field emission cannot be achieved [8]. The growth method used by Dijon *et al* leads to better electrical contacts but requires high temperatures (500–600 °C) which are not easy to obtain for a very large glass plate. Actually, in order to be competitive with the current liquid crystal display technology, similar sized glass plates have to be processed ($\sim 2.2 \times 2.5 \text{ m}^2$ for eighth-generation substrates).

Another drawback common to both technologies is that the emission site density is neither maximized, nor controlled. The carbon nanotubes are not vertically aligned and the uncontrollably small spacing between neighbouring emitters leads to high screening effects, which automatically reduces the emission site density. The field enhancement effect is the basis of field emission devices: the effective electric field at the apex of the emitters is equal to the applied electric field times the field enhancement factor β . In fact, electric fields above $3000 \text{ V } \mu\text{m}^{-1}$ are required at the apex to obtain field emission. Neither of the two previously described methods can control the tip geometry, as well as the orientation and the emitter density of the emissive film. As a consequence the emission site density, which is a crucial parameter for field emission display brightness and uniformity, is low [9], and does not allow one to fabricate very high quality displays.

We have already proposed an alternative field emission array technology, that makes use of metallic nanowires (NWs) instead of CNTs [1]. NWs also exhibit high aspect ratios (length in the μm range and radius around a few tens of nm). One of the major advantages of NWs compared to CNTs is the possibility to grow them by electrodeposition in a highly controlled nanoporous template. Such membranes are also often called nuclear track filters or screen membranes. These commercially available (Nuclepore, Poretics, Cyclopore, Osmonics, and Millipore) filtration membranes are usually prepared from polycarbonate or polyester. Electrodeposition is performed at atmospheric pressure and room temperature, and is compatible with very large surfaces. Using an ion track-etched template, we can grow vertically oriented metallic NWs with an excellent control of shape, orientation and density. In this case, a random distribution of the nanowires is obtained on the substrate but with a perfect control of their density. Here, we have chosen to grow NWs to a density of 10^7 cm^{-2} , corresponding to a minimum screening effect and a maximum emission site density as demonstrated by simulation [9].

In this paper we describe the fabrication of arrays of metallic nanowires with optimized characteristics (density, material, length, and diameter) for field emission application. We first present nanowire growth by electrodeposition into nanoporous polycarbonate film deposited on silicon substrates. Then, the field emission and total energy distribution (TED) measurements performed on as-grown metallic nanowires are extensively described. In particular, we detail their complex emission behaviour: an ‘activation’ of the emission is first required at high field, after which the electron energy distribution is composed of many peaks and the emission current is highly unstable. A model is presented to explain

Table 1. Chemical composition of the electrolytes.

Material	Electrolyte bath
Co	0.85 M (CoSO_4 , $7\text{H}_2\text{O}$) and 0.5 M H_3BO_3
Ni	0.5 M (NiSO_4 , $7\text{H}_2\text{O}$) and 0.5 M H_3BO_3
Cu	0.2 M (CuSO_4 , $5\text{H}_2\text{O}$), 0.1 M H_2SO_4
Rh	Rhodium S_2 (2 g l^{-1} Rh) Metakem GmbH

this behaviour, which is due to the presence of an oxide layer on the nanowire surface. Finally, we describe a simple *in situ* emitter treatment by ion bombardment that removes the oxide layer and leads to stable and reproducible field emission characteristics.

2. Nanowire growth

To fabricate arrays of vertically aligned nanowires, we used the template method, which consists of the controlled filling of nanopores of a track-etched polymer film by electrodeposition. We first deposit successively Ti, Pt and Au thin films by evaporation (50, 100 and 10 nm thick respectively) on a $300 \mu\text{m}$ thick n-doped Si(100) wafer to ensure good conductivity for electrodeposition. Then, we spin-coat a $3 \mu\text{m}$ thick polycarbonate layer on top of this substrate, which is subsequently irradiated with 200 MeV argon ions to a dose of 10^7 cm^{-2} , thus creating an array of linear ion damage tracks in the polycarbonate film. After UV sensitization, the samples are etched into a NaOH aqueous solution, which reveals the ion tracks and yields straight and homogeneous nanopores. As irradiation is performed through a 3 mm diameter mask (for easy measurement in our field emission vacuum vessel—see below), the pores are localized in a $\sim 7 \times 10^{-2} \text{ cm}^2$ area in the middle of the samples. The deposition is monitored by an EG&G model 263A potentiostat/galvanostat apparatus. To ensure good homogeneity of the growth rate and thus of the wire length, the deposit is performed in a pulse mode.

Electrodeposition of metal within the pores is performed until the nanowire length approaches the polycarbonate layer thickness (here $3 \mu\text{m}$). This is easily controlled by the $I(t)$ (current versus time) electrodeposition curve [10]. Finally we dissolve the polycarbonate layer and an array of vertically aligned metallic nanowires then remains on the substrate. As quoted above, the nanowire features as well as the array density are fully controlled. The pore density is defined during the irradiation phase by the ion dose (here 10^7 cm^{-2}), and the pore size (here 80 nm) is defined by the etching conditions. The nanowire length is monitored by the polymer layer thickness (pore length) and the growth time. Finally, the chosen nanowire material is obtained by a proper choice of the chemical solution used for the electrodeposition (see table 1).

The polycarbonate templates have been used to successfully grow Co, Ni, Rh, and Cu nanowires. The density, length and diameter of nanowires are those corresponding to the template design in all cases. Typical images of nanowire-covered substrates are shown in figure 1.

High-resolution transmission electron microscopes (Philips CM30 at 300 keV and a Hitachi Topcon at 200 keV) were used to characterize the structure of the cobalt nanowires.

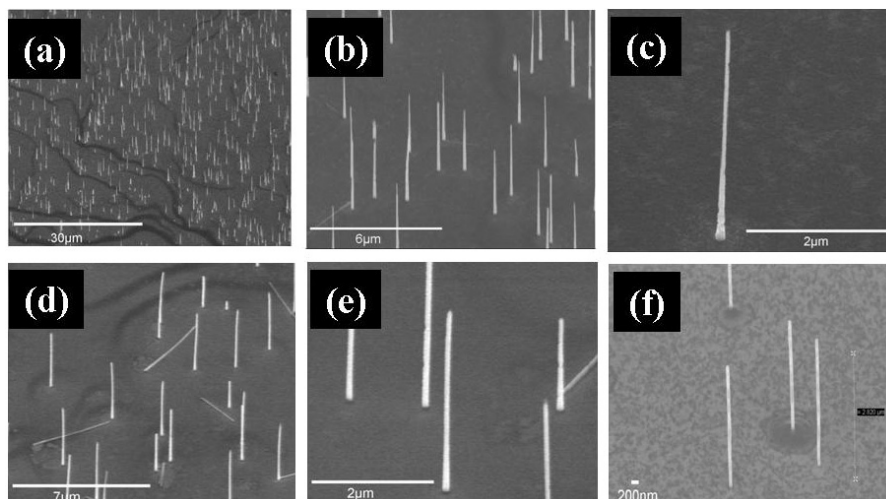


Figure 1. Scanning electron microscopy (SEM) images of arrays of metallic nanowires with a height of around $3\ \mu\text{m}$, a diameter of $80\ \text{nm}$ and a density of $10^7\ \text{cm}^{-2}$ obtained by electrodeposition into a nanoporous polycarbonate layer. (a)–(c) Three images of an array of cobalt NWs at three different magnifications. (d) Nickel NWs, (e) copper NWs, and (f) rhodium NWs.

The studies show that the diameter of nanowires is very uniform. The electron diffraction patterns indicate that the structure of nanowires is close-packed hexagonal. It is known that the crystallographic structure of the nanowires depends on the pH of the electrolyte [11], and the hexagonal structure is the one expected for the pH value of 4.5 used here. Transmission electron microscopy (TEM) images of the cobalt nanowires are shown in figure 2.

The TEM images show polycrystalline structures with nanosized Co crystallites packed randomly in the wires. Indeed, the electron diffraction pattern in figure 2(c) is composed of both a group of concentric rings and intense spots, indicating the polycrystalline structure at the macroscopic scale. To support this analysis, in figure 2(d) bright-field (BF) and dark-field (DF) TEM images of Co nanowires are shown, respectively, revealing the nanowire structure to be polycrystalline with nanosized Co crystal grains, separated by grain boundaries, along the nanowire direction.

3. Field emission measurements

3.1. Field emission from as-grown nanowires

Field emission was performed with nanowires of different materials, for which similar behaviours were observed. The field emission measurements presented below are those from the cobalt nanowires.

Field emission measurements were carried out (in a triode configuration) in an ultra-high vacuum chamber evacuated to base pressure of $\sim 10^{-9}$ Torr (vacuum system #1). The extraction grid consists of a $100\ \mu\text{m}$ thick n-doped silicon grid with a transparency of 20%. It is isolated from the substrate thanks to a $110\ \mu\text{m}$ thick silica spacer. A phosphor screen is used as the anode to observe the emission patterns and measure the emitted current. The expected theoretical emission current

is given by the Fowler–Nordheim relationship (1):

$$I(E) = S \frac{a}{\Phi} (\beta E)^2 \exp\left(-\frac{b\Phi^{3/2}}{\beta E}\right) \quad (1)$$

where a and b are two constants, Φ is the work function of the emitting material ($\sim 5\ \text{eV}$ for Co), E is the applied electric field, β is the field enhancement factor and S the active emission area [12, 13].

The measurement consists in applying several cathode-to-grid bias cycles. In the first cycle, we observe a phenomenon of ‘emission activation’ with an abrupt emission increase (from ~ 0 to $20\ \mu\text{A}$ at $17\text{--}18\ \text{V}\ \mu\text{m}^{-1}$ applied electric field). This activation is observed in the area labelled 1 in figure 3. During the following bias cycles, we have observed a shift of the threshold voltage towards lower fields ($10\ \text{V}\ \mu\text{m}^{-1}$) and more reproducible $I(V)$ curves were obtained (area labelled 2 on figure 3). The emission current density reached $0.4\ \text{mA}\ \text{cm}^{-2}$ at an applied field of $25\ \text{V}\ \mu\text{m}^{-1}$, and the enhancement factor β was estimated to be around 230. Another feature appearing on the curve is the non-Fowler–Nordheim behaviour at high field (area labelled 3 on figure 3). This has already been shown for carbon nanotubes, and in that case it was attributed to a voltage drop that appears along the emitter or at the carbon nanotube/substrate interface [8].

3.2. TEM studies

TEM observations show the presence of an oxide layer at the surface of the nanowires that could explain the observed high field deviation from the Fowler–Nordheim behaviour. This layer cannot be a contamination layer because the thickness is uniform all around the nanowire. In addition, the high-resolution TEM image (figure 4(c)) allows us to clearly discriminate from an amorphous layer to a crystallized layer. Measurements of the inter-reticular distance of the layers that surround the Co nanowire give a value close to $0.25\ \text{nm}$, which corresponds to the $d(111)$ lattice spacing of cubic CoO. For Co

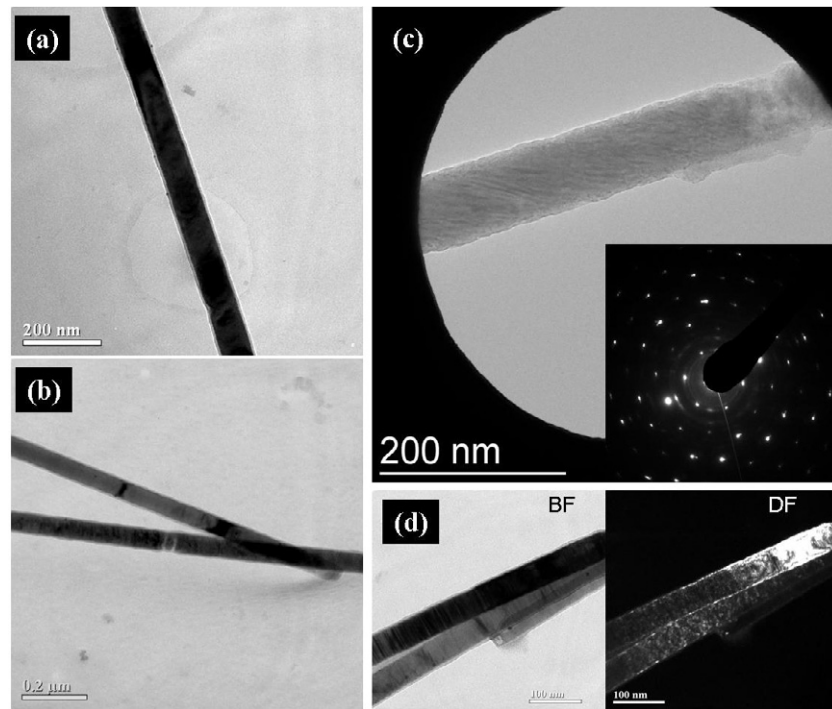


Figure 2. (a), (b) Transmission electron microscopy (TEM) images of as-grown cobalt nanowires showing the very uniform diameter. (c) TEM image of a Co nanowire. The inset plot is the electron diffraction pattern of the selected area. (d) Bright-field (BF) and dark-field (DF) images of Co nanowires. The dark-field image is formed from the diffraction spot from Co.

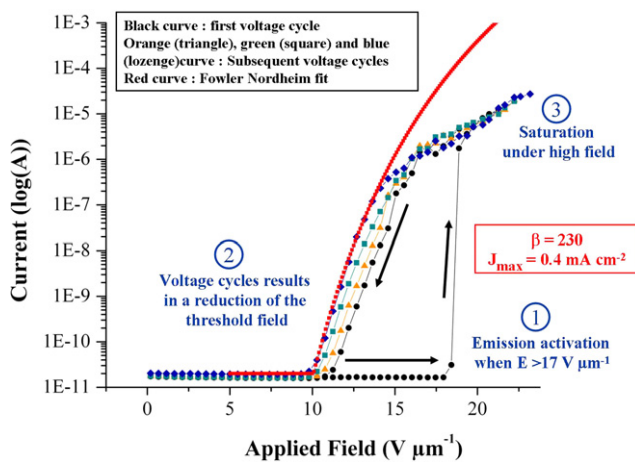


Figure 3. $I(V)$ field emission curves from cobalt nanowires. The red curve shows the Fowler–Nordheim fit. The arrows show the measurement sequence for the first cycle (black curve). We have observed three different regimes: emission activation in 1; reduction of the threshold field in 2; and saturation under high field in 3. (This figure is in colour only in the electronic version)

nanowires with a diameter of about 60 nm, an oxide layer with a thickness of ~ 10 nm was observed. TEM images of such Co nanowires are shown in figure 4.

3.3. Field emission energy spectroscopy

To confirm the role of the oxide layer, quasi-simultaneous field emission microscopy, current measurements and field

emission energy spectroscopy measurements were carried out in another (vacuum system #2) ultra-high vacuum chamber (1×10^{-10} Torr). Depending on the experimental procedures, emission characteristics at the level of a few emitters or even one emitter can be measured as discussed below. The field emission microscopy imaging is performed with a multichannel plate and a fluorescent screen. The spectra of total energy distributions were measured with an energy analyser through a probe hole subtending about 2° , whose nominal energy resolution is 10 meV. The procedure is described in more detail by Purcell *et al* elsewhere [14].

For the first measurement cycles and at the lowest currents in the pA range, the field emission microscopy imaging revealed just one or a few unstable emitting sites. The planar geometry means that there is only a slight magnification of the field emission microscopy image plane with respect to the emitting surface. However, this allowed distinguishing the different emitter sites as they are physically separated over the emitter plane. At higher currents, and particularly after the ion bombardment conditioning cycles discussed below, the number of emitter sites and their stability increased significantly.

The use of the probe hole combined with the selectivity in the field emission pattern means that the total energy distributions correspond to one emitter at this stage. The total energy distributions were complex. During the first measurement cycles the spectra realized at constant low bias (640 V for a current of 400 nA) showed, for each measurement, a single peak whose position is reproducible and shifted towards low energies compared to the Fermi level. In other words, there is a voltage drop somewhere between

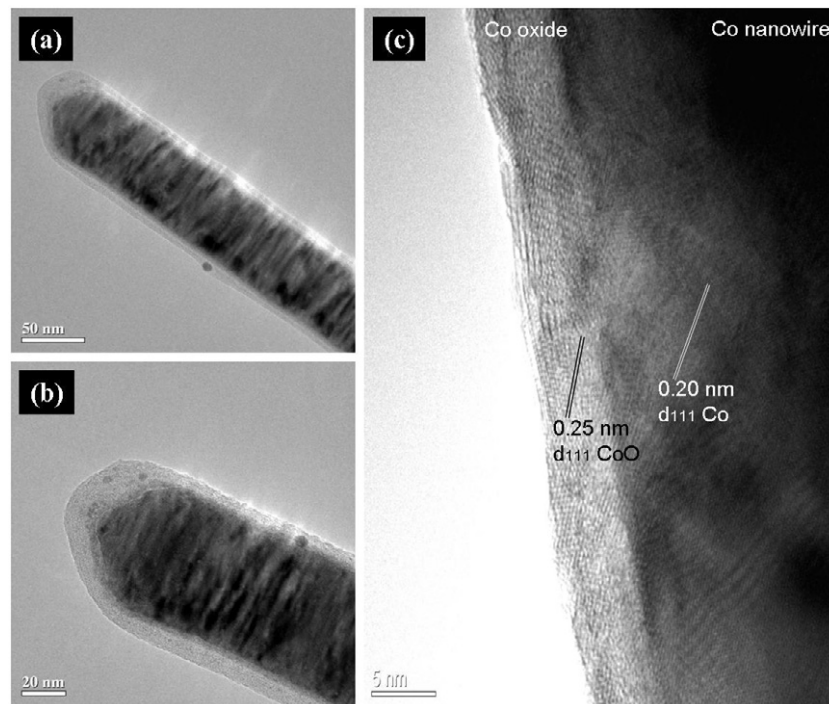


Figure 4. (a), (b) Transmission electron microscopy images of as-grown cobalt nanowires showing the presence of an oxide layer on surface. (c) High-resolution TEM image of a single nanowire showing that the Co nanowire is surrounded by a Co oxide layer.

the connection of the sample support and the emission zone. The width of the peak is of the order of 1 eV (figure 5(a)). When the voltage increases (700 V for a current of $2.7 \mu\text{A}$), measurements become unstable and not reproducible. The peak moves 3 eV towards the low energies and the width of the peak reaches 3 eV (figure 5(c)).

3.4. Model

In order to explain the set of measurements, we propose a model taking into account the oxide layer on the nanowire surface. The electron emission occurs only when some kind of ‘activation’ under high field has been applied. This necessity of activation can be explained by the presence of the oxide layer that inhibits the current emission at low electric fields. Under higher field, localized breakdowns appear in the oxide layer, thus creating conduction channels. During the emission, a voltage drop appears along these conductive ‘channels’, leading to an energy band bending in the oxide layer. Electrons are injected by the tunnel effect from the metal in the defective forbidden band of the oxide populated with electrons traps and they then fill the electronic states of the nanoprotusions. Electrons are extracted by field emission from these nanoprotusions (where the effective electric field is higher) to the vacuum. Under weak fields and low emitted current, the band bending is small and the energy of emitted electrons is close to the Fermi level (figure 5(b)). Under stronger fields a larger number of channels/nanoprotusions are created. Each emitter site of the nanowires contributes to the emission current and is characterized by a specific ΔE (with respect to the Fermi level) which depends on the local channel conductivity (figure 5(d)).

In order to obtain a reproducible and stable emission we have developed an *in situ* process to clean the nanowire by ion bombardment. Argon gas was introduced into the vacuum chamber (5×10^{-4} Torr) and then ionized by the field emission emitted electrons [15]. With this treatment the oxide layer present on the nanowire surfaces is removed by ion bombardment. Post-treatment energy distributions consisted of a single peak located at the Fermi energy regardless of the applied voltage (figure 5(e)). This is the signature of standard field emission from a metal, as shown schematically in figure 5(f)

3.5. Field emission measurement from as-grown nanowires after *in situ* treatment

A similar behaviour has been observed for collective measurements performed in vacuum system #1. Figure 6(a) presents the results before and after a somewhat different ion bombardment protocol. First, the emission current is measured up to a field of $\sim 15 \text{ V } \mu\text{m}^{-1}$. As emission has not been activated, no emission current is measured. Then the *in situ* ion bombardment treatment (hydrogen ions) is performed for 10–15 min with a hydrogen ion density of 10^{17} cm^{-2} and an energy of 600 eV. This treatment is realized with a Tectra 6530 ion beam. After treatment and for the same sample, a new series of measurements is performed. We obtain an emission current that is both stable and reproducible. No activation is required any more, and the emission is observed at low applied fields ($10 \text{ V } \mu\text{m}^{-1}$). The emission characteristic perfectly follows the Fowler–Nordheim law. This shows the possibility to collectively clean an array of metallic nanowires, thus eliminating the oxide layer and its deleterious effect on

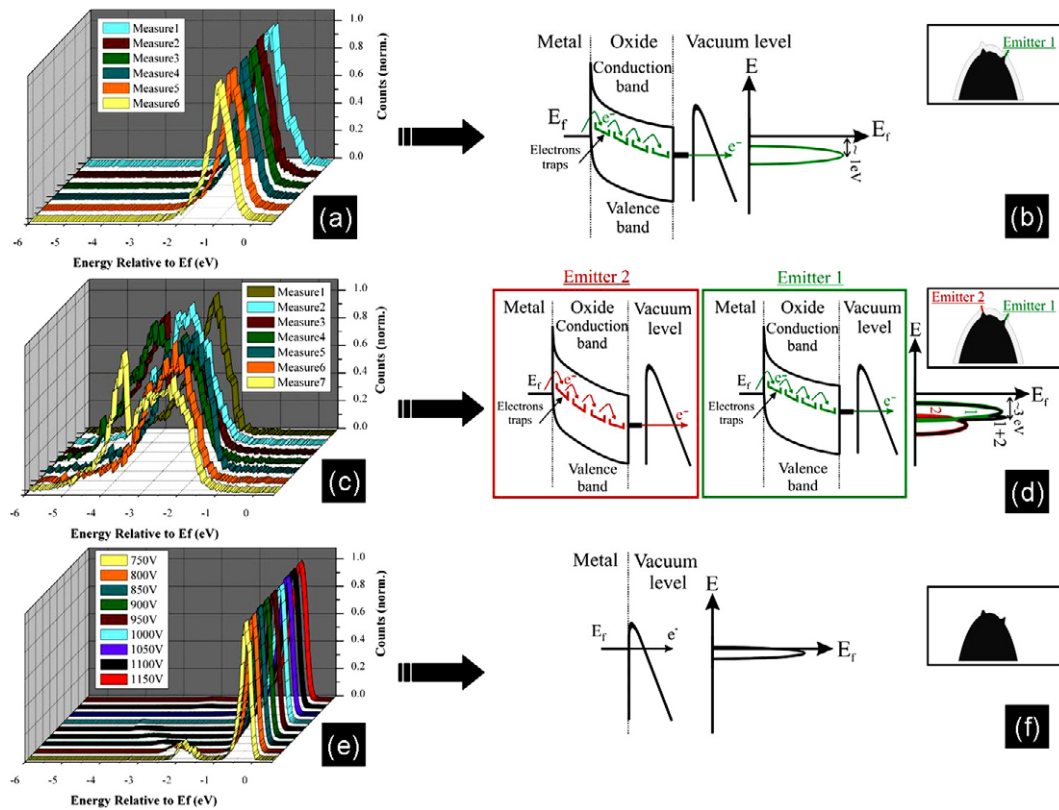


Figure 5. (a) The emitted electrons' energy distributions at 640 V for a current of 400 nA consist of a single peak whose position is reproducible and which shifts progressively towards low energies (compared to the Fermi level) as the applied voltage is increased. (b) Energy band diagram at low field explaining the emission characteristic. (c) Energy distribution at 700 V for a current of 2.7 μ A. Measurements become unstable and not reproducible. (d) Energy band diagram at high field explaining the emission characteristic. (e) Energy distribution for different voltages (750–1150 V) after the *in situ* treatment removing the oxide layer. (f) Energy band diagram after the *in situ* treatment and recovering of the traditional emission behaviour.

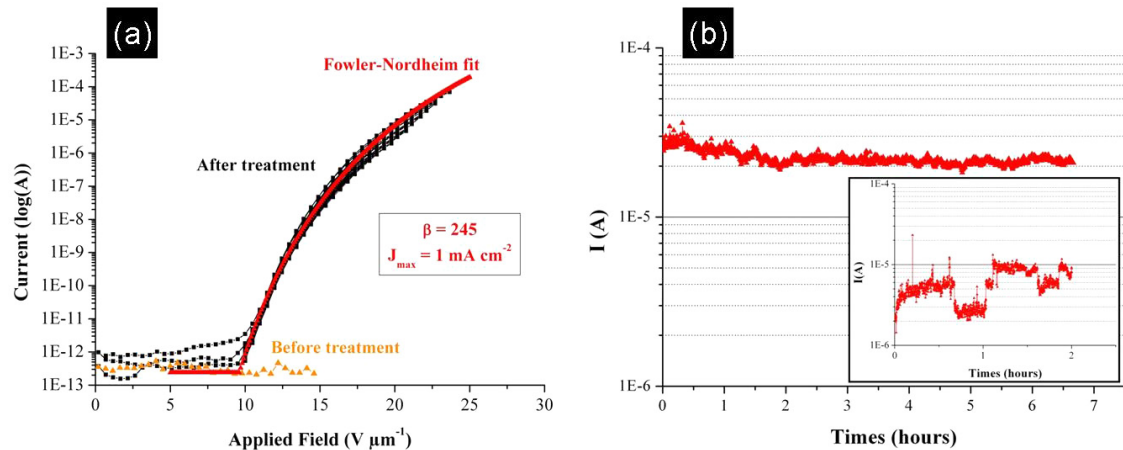


Figure 6. (a) $I(V)$ curves of cobalt nanowires after *in situ* hydrogen treatment. The red curve is the Fowler–Nordheim fit. First the emission current was measured up to 15 $V \mu m$ (yellow curve), and the measurement was stopped before the onset of emission activation. After treatment, a stable and a reproducible emission is obtained (black curves). (b) Field emission stability measurements over 7 h compared to results obtained on nanowires before treatment shown in the inset.

field emission behaviour. The field threshold is stable and constant even after several measurement cycles. Moreover, no saturation behaviour was observed over eight orders of magnitude of emission current. The emission current density

is about 1 mA cm^{-2} for an applied field of $25 \text{ V } \mu m^{-1}$, and the enhancement factor is estimated to be around 245. The current density is the range needed for field emission displays. Field emission stability measurements were realized after treatment

at 30 V μm^{-1} for a current of $22 \pm 2 \mu\text{A}$. Good emission stability was observed after treatment (for several hours), in contrast to the results obtained on as-grown nanowires (see inset in figure 6(b)).

4. Conclusion

In conclusion, metallic nanowires grown in supported nanoporous track-etched templates are a competitive solution for the realization of field emission displays (FEDs) or backlight units for liquid crystal displays. The growth process is performed at room temperature and atmospheric pressure, and is compatible with very large surfaces. With this process, we have obtained nanowires made of different materials (Co, Ni, Cu and Rh). The field emission and total energy distribution measurements have shown that, because of the presence of an oxide layer observed by TEM on as-grown nanowire surfaces, emission activation is necessary and the emission is unstable in that case. We propose here an *in situ* treatment with ion bombardment to collectively 'clean' the nanowire array and eliminate this oxide layer. After this *in situ* treatment, the NWs exhibit a stable and reproducible emission. Activation is no longer required. We have observed a good emission stability for several hours. This process can be potentially used for field emission displays, as the achieved current density is compatible with such an application.

Acknowledgments

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