Mass density of individual cobalt nanowires

L. Philippe,¹ B. Cousin,¹ Zhao Wang,^{1,2,a)} D. F. Zhang,¹ and J. Michler¹

¹EMPA (Swiss Federal Laboratories for Materials Testing and Research), Feuerwerkerstrasse 39, 3602 Thun, Switzerland

²LITEN, CEA-Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

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The mass density of nanowires is determined using *in situ* resonance frequency experiments combined with quasistatic nanotensile tests. Our results reveal an average mass density of 7.36 g/cm³, which is below the theoretical density of bulk cobalt. The results are discussed in terms of the measurement accuracy and the microstructure of the nanowires. © 2010 American Institute of Physics. [doi:10.1063/1.3299013]

During the last few years there has been increasing interest in the use of nanowires as key components in nano-electronic devices¹ due to their unique electrical and mechanical properties. In particular, mechanical resonance of nanowires is of great interest for basic research^{2,3} as well as for a wide range of applications in nanoelectromechanical systems, such as sensors, actuators, and field effect transistors.⁴⁻⁷ The fabrication of nanowires with low mass, tunable natural frequency and quality factor is crucial for the development of such nanodevices. The mass density of individual nanowires is one factor that determines resonance properties. It therefore plays a key role for potential applications of nanowires.

However, very little work has been done to date studying the density of nanowires, due to the difficulties of mass detection at the nanoscale. Densities of individual cross-sections can be measured using high-resolution microscopy,⁸ however it is almost impossible to measure the density along a whole wire using these techniques. Recently, resonance experiments have been used to study mechanical properties of free standing nanostructures.⁹⁻¹⁴ These experiments are based on the Bernoulli–Euler theory, in which the natural resonance frequencies (f_n) of a cantilevered beam can be written as follows:

$$f_n = \frac{(\beta_n)^2}{2\pi} \sqrt{\frac{EI}{mL^3}}, \quad (1)$$

where $\beta_{n=1,2,3,\dots} = 1.875, 4.694, 7.855, \dots$ are constants for the n th harmonic modes, E is the axial elastic modulus, I denotes the moment of inertia, m is the mass, and L stands for the beam length. In a number of recent resonance experiments on nanowires, E is calculated from this equation and m is usually derived from the bulk density value. However, the density of nanowires changes with different fabrication procedures.^{15,16} In this study, we report on a solution to this problem for free-standing nanowires combining resonance and nanotensile experiments. We use *in situ* resonance excitation of individual nanowires in a scanning electron microscope (SEM) to measure resonance frequencies, while the Young's modulus of nanowires is obtained from independent nanotensile experiments. The combination of these two experimental techniques allows us to calculate the mass density of individual nanowires using Eq. (1), unlike the techniques

measuring only local density on individual cross sections using high resolution microscopies.

Cobalt nanowires are synthesized using electrochemical deposition on templates. The full experimental details of the process can be found elsewhere.¹⁷ The following electrolytes have been used for the cobalt solution: CoSO₄ (1M), H₃BO₃ (0.7M), and NaCl (0.11M). The solution pH has been adjusted to 3.5. Extraction of nanowires from the template has been performed by gold layer chemical dissolution (I₂:2KI:10H₂O), followed by dissolving the polycarbonate membrane in dichloromethane.

Resonance experiments have been performed to measure the resonance frequency of free-standing samples. In the literature, vibration of nanowires was induced at one of their resonance modes by thermal vibration¹⁸ or electric fields.⁹ In this letter, vibrations of nanowires were induced by the oscillation of a piezoelectric actuator in a SEM chamber (Hitachi S-3600), in which samples were attached to a razor blade fixed on the piezoelectric actuator. Joints were made between the razor and nanowires by *in situ* electron-beam induced deposition of residual hydrocarbon in the SEM chamber. The amplitude-frequency curves were achieved by using secondary electron detection with a stationary beam near the sample. A peak of secondary electrons can be detected once the nanowires reach their maximal amplitude during the vibrations. In our measurement, we increased the SEM magnification to 200 000 and adjusted the spot of the electron beam to make it slightly defocused to increase the dynamic range by having more spatial interactions between the beam and the vibrating wires.^{19,20}

An example of our resonance experiments is shown in Fig. 1, in which we can see different stages of the vibration of a nanowire [(a)–(d)]. We can see that the wire vibrates at the fundamental harmonic mode and the maximum amplitude of deflection can be measured from SEM images. In Figs. 1(e) and 1(f), an overview spectrum was acquired by means of the stationary beam technique in which we locate resonance peaks by sweeping the excitation frequency through the full available measurable bandwidth up to 1.2 MHz and measure amplitude and phase response. We found that the average resonance frequency of these nanowires is about 1 MHz.

To measure the axial elastic modulus of these nanowires, quasistatic tensile tests have been performed using a micro-electromechanical system (MEMS)-based tensile-testing stage, which consists of a comb drive actuator, a force sen-

^{a)}Electronic mail: wzzhao@yahoo.fr.

FIG. 1. (Color online) [(a)–(d)] SEM images of the resonance of a free-standing cobalt nanowire ($L \approx 15 \mu\text{m}$) at a fundamental mode. Vibrations were induced by piezomechanical excitation and detected by measuring the secondary electron signal created by interactions between the wire and the electron beam. [(e) and (f)] a wide spectrum of the amplitude response which locates the peak in the vicinity of 868 KHz.

sor, and a gap in between. An individual cobalt nanowire was bridged over the gap by pick-and-place nanomanipulation performed inside a SEM and fixed at the two ends via focused electron-beam induced deposition (FEBID).²¹ A uniaxial voltage-controlled tensile force was applied to the specimen through the electrostatic actuator. The tensile load was measured from the displacement of the force sensor with a known spring constant. Series of high-magnification SEM images were taken during the tensile experiments from which the deformation of the specimen elongation could be extracted by image analysis with a program based on a cross correlation algorithm.²² Further details on the instrument and the experiments can be found in Ref. 23.

The nanostructure of electrodeposited cobalt nanowires was analyzed by using a transmission electron microscope (TEM). It has been found that these wires exhibit crystal orientation variations (see Fig. 2), and that the grain sizes vary roughly from 10 to 150 nm. These local variations can be due to fluctuations of metal concentration and pH value in solution during the synthesis processes which can reduce reaction kinetics during the deposition.^{17,24} From this nanocrystalline structure together with the potential presence of

FIG. 2. (Color online) TEM image with corresponding diffraction pattern of a cobalt nanowire. Inset: Pattern reveals that this cobalt nanowire exhibits variations of crystal orientations (polycrystalline). The plot on the pattern shows the intensity of the diffracted beams with respect to the diffraction angle.

TABLE I. Mass density $\rho(\text{g}/\text{cm}^3)$ and Q factors of nine cobalt nanowires versus the volume $V(\mu\text{m}^3)$. X: Unavailable data.

Sample	V	ρ	Q
1	0.231	9.237	X
2	0.245	7.030	589
3	0.305	8.383	451
4	0.365	6.431	X
5	0.442	8.886	X
6	0.510	6.982	341
7	0.821	5.728	457
8	0.830	6.895	338
9	1.133	6.694	453
mean	0.542	7.363	438

pores that can form during the electroplating process, density variations can be expected. The latter would also influence the elastic modulus^{25,26} and the quality factor.²⁷

The quality factor (Q) quantifies the energy dissipation to the environment in a vibrating system. In our case of high vacuum condition, Q mainly describes the dissipation to the supports. Here quality factors for the fundamental resonance mode of cobalt nanowires in high vacuum at room temperature were determined from the slope of the phase curve at resonance using the following equation:

$$Q = \frac{f_0}{2} \left| \frac{d\phi(f_0)}{df} \right|, \quad (2)$$

where $d\phi/df$ is the phase variation.^{28,29} The results of Q are shown in Table I. A good reproducibility of the quality factor measured for a given volume, as well as an expected increase of Q with V was observed in both sets of measurements. These results show the possibility to make nanowires with tunable quality factor by controlling the wire size. This is an important issue for applications of nanowires in nanoelectronics.

Eight cobalt nanowires were tested in the nanotensile experiments (see Ref. 23). The measured average value of the Young's modulus is 75.28 ± 14.6 GPa, which is much lower than that of the bulk (209 GPa). Possible reasons for the reduction in the Young's modulus are the structural defects (e.g., pores) and surface effects (e.g., surface oxide layer and contamination) in the nanowires. The defect-induced mechanical softening effects were previously reported for both nanostructures and bulk materials.^{26,30} Also, additional damage could be produced by the pick-and-place nanomanipulation of individual nanowires on the MEMS device. This may somewhat explain the scatter of the Young's modulus data reported in Ref. 23.

As shown in Eq. (1), the resonance frequency depends on the elastic modulus and the density of nanowires. If the cross section is considered as a cylinder $I = \pi d^4/64$, the frequency (f_0) of a fundamental mode can be written as a function of wire density (ρ), as follows:

$$\rho = \frac{d^2 \beta_0^4 E}{64 \pi^2 L^4 f_0^2}, \quad (3)$$

where d and L are the diameter and the length of nanowires, respectively. Putting the values of f_0 from resonance experiments and those of Young's modulus from tensile experiments into Eq. (3), we can calculate the average density of

each wire (see results in Table I). The average density value of our electrodeposited cobalt nanowires is about 7.36 g/cm^3 , which is about 83% of the bulk value (8.9 g/cm^3). This value, lower than the theoretical density, might be related to the low elastic modulus of the nanowires. We note that the cross-sectional shape variation of the nanowires³¹ can also result in errors in the density calculation using Eq. (3), and hence contribute to the data scattering of the density, e.g., deviations from the ideal cylindrical shape to conical pillars will considerably alter the prefactor up to a 25 times reduction of the elastic-modulus-over-density ratio.²⁸ It is therefore shown that the error using Eq. (3) could be large if the cross section shape changes a lot. Hence we have carefully chosen samples with a relatively uniform cross section shape (e.g., Fig. 2) to minimize this effect.

Following our error estimation approach taking into account the imprecision in the measurement of the dimensions, the estimated *maximum* error in an individual density value is approximately $\pm 45\%$, including $2 \times 3\%$ from the diameter, $4 \times 5\%$ from the length, 2% from the frequency, and 18% from the Young's modulus.²³ This error estimation is consistent to Ref. 28 since the wire dimensions were also measured in high-resolution SEM. The measurement is considered to be more accurate than that using SEM image analysis.¹⁴ The errors from the attachment is difficult to estimate since the substrate is not perfectly planar and the clamping depth of the nanowire into the substrate is difficult to be estimated. Variation in the mode constant β due to nonrigid clamping has been reported in the literature.³² We believe that the β variation should be partially responsible for the ρ data scattering. Furthermore, the redeposition of FEBID contaminants onto the nanowires could, as well, affect the resonance frequencies.

In conclusion, we have measured the density of electrodeposited cobalt nanowires, combining nanoresonance and nanotensile experiments. This combination allows calculating the mass density of individual nanowires from the experimentally measured resonance frequency and elastic modulus, using a classical formula of elasticity theory. Together with an independent measurement of the elastic modulus by nanotensile test, average density of nanowires around 7.36 g/cm^3 is found. These results are expected to be useful in particular for the potential applications of nanowires in nanoelectronic devices or nanoelectromechanical systems. The lack of observable porosity in the TEM images is in agreement with the measured density from these experiments being not too far below (83% of) the bulk value for polycrystalline Co nanowires. Clamp compliance appears likely to be significantly reflected in the values of modulus (measured $E \approx 37\%$ of bulk material value) in both nanotensile as well as resonance (through β_n) measurements and this will be an area for improvement in our future work.

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