Dose and energy dependence of mechanical properties of focused electron-beam-induced pillar deposits from Cu(C₅HF₆O₂)₂

V Friedli¹, I Utke¹, K Mølhave² and J Michler¹

¹ EMPA, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH-3602 Thun, Switzerland
² Department of Micro and Nanotechnology, Technical University of Denmark, Building 345e, DK-2800 Kongens Lyngby, Denmark

E-mail: ivo.utke@empa.ch

Received 22 June 2009, in final form 4 August 2009
Published 28 August 2009
Online at stacks.iop.org/Nano/20/385304

Abstract
Bending and vibration tests performed inside a scanning electron microscope were used to mechanically characterize high aspect pillars grown by focused electron-beam- (FEB) induced deposition from the precursor Cu(C₅HF₆O₂)₂. Supported by finite element (FE) analysis the Young’s modulus was determined from load–deflection measurements using cantilever-based force sensing and the material density from additional resonance vibration analysis. The pillar material consisted of a carbonaceous (C-, O-, F-, H-containing) matrix which embeds 5–10 at.% Cu deposited at 5 and 20 keV primary electron energy and 100 pA beam current, depending on primary electron energy. The Young’s moduli of the FEB deposits increased from 17 ± 6 to 25 ± 8 GPa with increasing electron dose. The density of the carbonaceous matrix shows a dependence on the primary electron energy: 1.2 ± 0.3 g cm⁻³ (5 keV) and 2.2 ± 0.5 g cm⁻³ (20 keV). At a given primary energy a correlation with the irradiation dose is found. Quality factors determined from the phase relation at resonance of the fundamental pillar vibration mode were in the range of 150–600 and correlated to the deposited irradiation energy.

1. Introduction

The increasing importance of gas-assisted focused electron-beam- (FEB) induced deposition as an extremely flexible, maskless direct-write nanofabrication technique for three-dimensional prototyping at sub-100 nm scale demands in-depth studies of the mechanical properties of such obtained deposits. Such studies will be useful for progress in rapid prototyping of nanowire or nanotube hybrid structures which requires in situ bonding after correct placement in an electron microscope [1–5]. In addition FEB-fabricated scanning probe microscopy sensors, like magnetic [6], thermal [7], optical [8, 9] and scanning tunnelling tips [10–12], as well as grippers [13] and nanoimprint tools [14] require analysis of their mechanical properties and their dependence on deposition parameters in order for further mechanical optimization. Mechanical studies are also important for small deposits obtained from gas-assisted focused ion-beam- (FIB) induced deposition such as grippers [15] and biocell surgery [16]. In contrast to gas-assisted FIB deposition, FEB-induced deposition proceeds without contamination (no ion implantation into the growing deposit) and with better resolution. The smallest deposit dimensions so far obtained with FEB were 1 nm dot deposits [17] and 5 nm for freestanding pillars [18].

FEB (and FIB) deposits obtained from carbon-containing organometallic molecules feature a composite structure, i.e. nanocrystalline metal grains embedded in a carbonaceous matrix [19]. Such a composite structure is often advantageous for sensors in terms of magnetic, optical or electric...
functionality (which is supplied by the dispersed metallic nanocrystals) and simultaneous mechanical and chemical stability supplied by the carbonaceous matrix. Evidently, the mechanical properties, such as stiffness, density, strength, toughness and adhesion, must be determined experimentally since no data is available from template bulk materials. Both static and dynamic mechanical test methods provide an effective way to characterize materials at the micro- and nanomechanical level [20]. For one-dimensional pillar-like nanostructures, including nanowires and nanotubes, measurement techniques based on bending and vibration tests are well suited. Of note, in mechanics the term ‘pillar’ often relates to a structure under compressive load. In this paper the structures are subjected to bending and vibration: however, we adhere to the term ‘pillar’ as the FEB and FIB literature refers to this term when a high aspect ratio structure is deposited coaxially within a finely focused electron beam. The integration of such mechanical test set-ups in a scanning electron microscope (SEM) has proven to be a successful approach to allow for visual observation of tests on individual nanostructures [21]. Furthermore, the SEM is the ideal instrument to determine the three-dimensional geometry of the tested structures, which is a crucial task in obtaining accurate mechanical properties.

Density and Young’s modulus measurements of FEB- or FIB-deposited pillars are still very rare (FIB: [22–27], FEB: [28–30]) and the precision of the methodology not yet quantitatively determined. In the following we report on bending and vibration tests inside an SEM to measure the force constant, resonance frequency and, for the first time, the quality factor of pillars deposited by FEB-induced deposition from the organometallic precursor (Cu(C₅H₆F₆O₂)₂·xH₂O, copperhexafluoroacetylacetone (hfa) hydrate, CAS: 155640-85-0). Furthermore, the values of Young’s modulus and the density of the deposited materials were extracted by finite element (FE) analysis and we discuss the influence of non-cylindrical pillar geometries. We compare our results to available literature data and discuss the dependence of irradiation dose, deposited energy and primary electron energy on the mechanical properties of the pillar deposits.

2. Theory

For single clamped cylindrical pillars with elastically isotropic material properties, uniform diameter, d, and length, l, mechanical theory (Euler–Bernoulli beam model for bending deflection, which neglects shearing and rotary inertia) provides a formulation of the Young’s modulus in terms of the pillar’s force constant, k₄, as [31]

$$E = \frac{64}{3\pi d^4} k_4.$$  

(1)

In addition the velocity of sound in the material relates to the resonance frequency of the fundamental flexural mode, f₀, as [32]

$$\sqrt{\frac{E}{\rho}} = \frac{7.148}{d} f_0.$$  

(2)

Deviations from the ideal cylindrical shape will considerably alter the pre-factor. For instance, for conical pillars (2) changes to $\sqrt{\frac{E}{\rho}} = 2.883l^2/d_{base,f0}$ [33], corresponding to a 5× reduction of $\sqrt{E/\rho}$ for a conical pillar with diameter $d_{base} = 2d$ compared to a uniform and otherwise equivalent pillar. This highlights that the shape variation of the width must be correctly input into the model and the dimensions accurately measured. Nonaka et al used an analytical model based on a polynomial fit of the diameter versus length variation of non-uniform pillars and solved the free vibration equation by the variation principle [34]. We used static and dynamic FE analysis to model the load–deflection and vibration behaviour of cylindrical pillars with non-uniform diameter.

3. Experiment

3.1. Sample preparation

For mechanical characterization of FEB-deposited materials, pillars with aspect ratios >30 were deposited from the precursor Cu(C₅H₆F₆O₂)₂ (see figure 1) in an SEM equipped with a thermal tungsten emitter and a homebuilt gas injection system (GIS). The FEB irradiated the substrate at normal incidence and the pillars grew vertically into the stationary beam. All depositions were performed on an Si substrate with a native oxide at a probe current of 100 pA measured in a Faraday cup and at acceleration voltages of 5 and 20 kV. The 5 kV series in figure 1 shows that the best focus conditions gives the highest growth rate. The local precursor flux to the deposition site was determined as $1.3 \times 10^{17}$ cm⁻² s⁻¹ from the measured precursor mass loss rate and Monte Carlo simulations [35] of the gas flow through the tube nozzle of

Figure 1. FEB deposits grown normal to the substrate in continuous spot mode for 30 min. SEM observation with 68° substrate tilt. Deposition conditions: 100 pA probe current, acceleration voltage is indicated. Precursor: Cu(C₅H₆F₆O₂)₂. Note the non-uniform diameter of pillars 3,4 and 5. For pillar 5 the variation of the base and the top diameter relative to the indicated minimal diameter, $d_{min} = 238$ nm, is +15% and +36%, respectively.
the GIS in the molecular flow regime. The backpressure in the vacuum chamber during the deposition experiments was $3 \times 10^{-3}$ mbar.

The pillars were grown at $>10 \, \mu m$ lateral pitch distance on the substrate which avoided proximity effects [36] and additional deposition [37]. It has been experimentally observed that slight bending is induced during observation of the pillars in a field-emission gun SEM, probably due to surface stress by a deposited contamination layer [38]. The vertical deposition rate, averaged over the entire deposition time, was of the order of $7–9 \, nm \, s^{-1}$ at both 5 and 20 kV. Although the deposition time was 30 min for all pillars, a difference in deposit height is observed which is attributed to focus adjustments between subsequent depositions. The 5 kV pillars show side roughness whereas the pillars grown at 20 kV have smooth surfaces. This phenomenon has been reported in the literature several times but is currently not fully understood [39]. The influence of this roughness on the mechanical measurements was considered to be negligible.

3.2. SEM integrated bending tests

SEM integrated bending experiments for the determination of stiffness relies on physical interaction between the pillar and a micromachined reference cantilever used as the force sensor. We used an SEM integrated nanomanipulation set-up composed of two vacuum-compatible positioning units. For the approach towards the pillar sample, the cantilever was mounted on a three-axes nanomanipulator with two rotational and one linear degree of freedom (MM3A, Kleindiek Nanotechnik, Reutlingen, Germany). The sample was mounted on a three-axes Cartesian nanopositioning stage with integrated capacitive position sensors (P-620 series, Physik Instrumente (PI), Karlsruhe, Germany) which provide close-loop positioning with sub-nanometre resolution. The entire setup was mounted on the SEM stage such that the pillar axis was at an angle of 85° with the FEB.

In a bending test as depicted schematically in figure 2(a) the load–deflection relation at the contact position is given by

$$F = k_i \Delta z_i = k_d \Delta z_d,$$

where $F$ is the force component acting perpendicular to the sample axis, $k_i$ and $k_d$ are the force constants, and $\Delta z_i$ and $\Delta z_d$ are the deflections of the reference cantilever and the sample, respectively. For the experiments a reference cantilever was chosen which had a force constant close to the material and supports that the experiments considering variations in thermally grown thin film SiO$_2$ properties of $\Delta E_{SiO_2} = 0.1 E_{SiO_2}$ and $\Delta \rho_{SiO_2} = 0.03 \rho_{SiO_2}$. The corresponding cantilever thickness is found as $h_i = \frac{1.787 l_1^2 \sqrt{\rho_{SiO_2}}}{E_{SiO_2} f_0} = 0.96 \, \mu m$, which is close to the nominal value of 1 $\mu m$.

A bending test on one of the pillars is shown in figures 2(b) and (c). Generally, pushing the sample against the force sensor (+$\Delta z$ direction) deflected both the pillar and the cantilever. In all experiments the deflection $\Delta z_d$ was kept <10% of the pillar length. Additional experiments confirmed that the bent pillars flexed back to their initial unstrained position upon release of the bending load by retracting the reference cantilever and thus no plastic deformation occurred. The quantification of bending tests was performed based on image post-processing of video data captured by SEM imaging during the tests. A cross-correlation algorithm detected the location of a previously defined image detail and the corresponding coordinates were saved in the video time line sequence. Both the root and the pillar location were traced using this technique and revealed (i) the relative stage displacement $\Delta z$ and (ii) the pillar deflection $\Delta z_d = \Delta z - \Delta z_i$ during the bending test experiment. The data of one experiment presented in figure 3 shows the measured pillar deflection in terms of the applied load $F$. The negative load corresponds to a retraction of the pillar from the cantilever beyond their unstrained position. In this retraction regime the pillar–cantilever contact is maintained by attractive electrostatic forces induced during the observation with the electron beam. The reproducibility of iterative bending measurements on the same pillar was very high, which confirms that deflections <0.1$\Delta z_d$/1 did not influence the stiffness of the material and supports that the experiments are performed within the elastic deformation limit. The
displacement noise observed in the post-processed deflection data originating from noisy SEM images was maximally one pixel which corresponded to a position accuracy of 20 nm. With the reference cantilever used a force resolution of 0.4 nN was obtained.

The pillar force constant, $k_d$, is determined using (3). The tilt angle between the cantilever and the pillar sample was kept minimal to minimize errors from this source [2]. In some cases we observed nonlinear deflection behaviour in the pillar–cantilever retraction regime. We speculate that such a behaviour results from a slightly bi-stable behaviour of the cantilever due to its particular very slightly curved shape which results in a nonlinear force constant at retraction loads larger than about $-2 \text{nN}$ from its unstrained position at $F = 0 \text{nN}$ (see figure 3). Of note is that the results of the deflection test are predominantly influenced by the properties of the electron-impact-dissociated base material where the highest strain occurs [42].

3.3. SEM integrated vibration tests

In a vibration test the pillar samples were mechanically excited at their fundamental resonance mode as shown in figure 4. The vibration amplitude maximum which determines the resonance frequency, $f_0$, was detected in two ways inside the SEM: the overall modal shape and the absolute maximum deflection amplitude for a given excitation amplitude was visualized by SEM imaging and the frequency spectrum was taken by the secondary electron (SE) signal through the interaction of a stationary beam with the vibrating structure [23]. If the stationary electron beam irradiates the maximum amplitude position, a peak in the integrated SE signal is detected at resonance while sweeping the excitation frequency. This is due to the increasing dwell time of the vibrating sample inside the beam. Best results were achieved by slightly defocusing the stationary electron beam which increased the dynamic range of the technique due to a spatially increased interaction between the beam and the vibrating pillar. Phase locking of the time-resolved SE and excitation signal allows extracting the response of amplitude and phase at resonance from the noisy SE signal. The position of the peak maximum corresponds to the resonance frequency $f_0$. It should be noted that the acquired SE signal due to the pillar deflection is, in general, not linear with the pillar’s vibration amplitude, e.g. due to edge effects generating artefacts in the SE signal and due to the limitation of the dynamic range at low amplitudes resulting from the SE signal’s strong dependence on the FEB position relative to the deposit. Hence, errors are inherently introduced when measuring the frequency peak full width at half-maximum, FWHM, and determining the quality factor with the formula $Q_A = \sqrt{2} f_0 / \text{FWHM}$. Calculating the quality factor of the pillar vibrations using the phase slope at resonance $Q_P = f_0 / 2|d\phi/df|_{f_0}$ avoids such errors. For example, in figure 4(b) the error is $Q_A/Q_P = 1.5$.

A typical resonance test is shown in figure 4(b). In a first step an overview spectrum was acquired with the stationary beam technique to roughly locate resonance peaks by sweeping the excitation frequency through the full available detection bandwidth of up to 1.2 MHz. Secondly, close-up spectra were acquired at the frequencies of interest. In all the resonance test experiments the excitation amplitude was adjusted to limit the deflection amplitude peak to <10% of the pillar length to avoid plastic deformation.

In some of the experiments we observed two resonance modes vibrating along the orthogonal principal axes. To detect all resonance modes, spectra were routinely acquired along two perpendicular directions with the stationary beam technique at top-view incidence. Once the orthogonal directions of the polarized resonance modes were identified the stationary electron beam was positioned at 45° relative to these directions. This allowed detecting all peaks in a single frequency sweep as shown in figure 5. If two peaks were observed we used the average frequency to evaluate (2).

Orthogonal resonance modes probe the geometrical deviations from the ideal straight cylinder shape. They can be attributed to both a non-circular pillar cross section and a curved pillar shape [43]. Theory predicts two orthogonal resonance modes for a pillar with elliptical cross section, the frequency ratio being proportional to the ratio of the two principal diameters. From our FE simulations we found that the intrinsic curvature of a pillar, modelled as a torus segment, splits up the resonance into an in-curvature-plane mode and a mode normal-to-curvature-plane. The FE results proved an approximation formula $f_{\text{deflected}}/f_{\text{straight}} \approx \sqrt{1 + 0.04l^2/R^2} [44]$ for a pillar with length $l$ and radius of curvature $R$, to be consistent to within a few %. Accordingly, a pillar which is curved by 20% from straight at its top ($R/l = 2.5$) has an in-curvature-plane resonance frequency which is shifted by +0.32% with respect to the straight pillar. Our FE analysis further predicts in this case a splitting of the two orthogonal frequencies by about 0.23%.
Figure 4. (a) Measurement principle in a piezo-driven resonance experiment based on the stationary beam technique. Locking the sample deflection signal from the secondary electron (SE) detector to the excitation signal reveals the deflection amplitude \( A_d(f) \) and the phase characteristics \( \phi(f) \) at resonance. (b) Spectrum of the fundamental resonance of pillar 5. Insets: top-view SEM images show the slightly tilted pillar excited at off-resonance and at resonance. The SE deflection signal is locked to the excitation in the range between 565 and 568 kHz. The inset on the right shows a full range spectrum up to 1 MHz of the amplitude response which locates the peak at \( f_0 = 566.6 \text{ kHz} \). The phase slope at resonance corresponds to a quality factor of 274.

Figure 5. The stationary beam technique detects polarized vibrations as a double amplitude peak and a 90° phase shift between the two resonances in the secondary electron spectrum. The insets illustrate the corresponding orthogonal vibration directions.

3.4. Chemical composition

The composition of the pillars measured by energy-dispersive x-ray spectroscopy (EDX) is given in terms of a pseudo-binary compound \( \text{Cu}_x\text{M}_{1-x} \), where \( \text{M} \) denotes the carbonaceous matrix. For example, the precursor molecule in this study \( \text{Cu}(\text{C}_5\text{H}_6\text{F}_6\text{O}_2)_2 \) is \( \text{Cu}_{0.03}\text{M}_{0.97} \), where \( \text{M} = (\text{C}_5\text{H}_6\text{F}_6\text{O}_2)_2 = (\text{Cu}_{0.36}\text{O}_{0.14}\text{F}_{0.43}\text{H}_{0.07}) \). Under electron irradiation the adsorbed molecule is fragmented, volatile desorbed fragments are pumped away and the deposit composition becomes \( \text{Cu}_{0.1}\text{M}_{0.9} \) \( (\text{M}_{0.9} = \text{Cu}_{0.6}\text{O}_{0.22}\text{F}_{0.08}) \) for 5 keV electrons and \( \text{Cu}_{0.06}\text{M}_{0.94} \) \( (\text{M}_{0.94} = \text{Cu}_{0.7}\text{O}_{0.2}\text{F}_{0.04}) \) for 20 kV electrons. The hydrogen content (which is not detected by EDX) can generally be neglected due to \( x_\text{H} \text{M}_\text{H}/\text{M}_\text{d} < 1\% \), for typical hydrogen contents \( x_\text{H} < 17\% \) in FEB deposits [46]. The accuracy of the measured elemental composition, used for subsequent error analysis, is within 5%.

The Young’s modulus and the density were then determined such that the model calculations were adjusted to match the experimental results. The optimum mesh grid was determined by adjusting the grid density until the FE results varied less than 0.01% when compared to a further simulation run using a finer mesh grid. The shape of the pillars was determined from SEM images and modelled by a spline function connecting measurements.

3.5. Finite element analysis

The experimentally determined values of the pillar force constant, \( k_d \), and resonance frequency, \( f_0 \), as well as the experimentally determined pillar shape were the input for FE analysis executed using the software ANSYS Multiphysics. The Young’s modulus and the density were then determined such that the model calculations were adjusted to match the experimental results. The optimum mesh grid was determined by adjusting the grid density until the FE results varied less than 0.01% when compared to a further simulation run using a finer mesh grid.
of the pillar diameter at typically five positions distributed along the pillar axis such that minimum and maximum diameter values were included. Such rotational-symmetry pillar models represent a smooth shape of the pillar; they deviated less than ±5% from the pillar shapes observed in the SEM images. Pillars were imaged from two perpendicular directions to exclude projection errors. We found that the pillars had an ellipticity of 1–2%. Furthermore, the silicon substrate was taken into account in the FE model to such an extent that the side and bottom surfaces did not influence the results. The model assumed a homogeneous density and Young’s modulus along the pillar which is reasonable with respect to our EDX measurements showing no difference in pillar composition between the base and apex part of the pillar.

4. Results and discussion

The details of the FEB-deposited pillars and the results of the determined Young’s modulus and density are compiled in table 1.

4.1. Irradiation dose and deposited energy

In the following we would like to discuss the mechanical properties listed in table 1 as a function of irradiation dose and deposited energy. Since we measured the composition and density of the deposits we can relate these parameters directly to the number of deposited atoms. This gives a much better idea at the atomistic level, i.e. how many electrons or amount of energy a deposited atom has received during FEB deposition; and, furthermore, it is a dimensionless representation which allows for easy comparison of other materials deposited by FEB.

The dose in units of impinging electrons per deposited atom is [45]

$$D = \frac{I_P t/e_0}{V_d \rho_d N_A / M_d},$$

where $V_d$ is the deposit volume, $I_P$ the probe current, $t$ the deposition time, $e_0$ the electron charge and $N_A$ Avogadro’s constant. The molar mass of the deposit, $M_d$, is determined from EDX composition measurements (see section 4.2). All other parameters were also measured and the standard deviation in this method is $\sigma_D = 0.07 D$. Of note, the inverse of (4) gives the deposition yield $Y_D = 1/D$ (which is proportional to the adsorbed density of non-dissociated molecules $n$ in the irradiated region and the electron-impact dissociation cross section $\sigma$, $Y_D = n \sigma$). From classical resist-based e-beam lithography it is known that, in a given dose range, the irradiation dose is proportional to the number of possible chemical reactions excited by electrons inside the deposit (or resist), such as molecular dissociation, bond formation or electron-stimulated desorption.

The energy $W$ deposited from the primary electrons inside the pillar apex was MC simulated with MOCASIM [47], which uses the Bethe stopping power approximation [19] along the electron trajectories (see figure 6). On average, 3.3 keV and 2.1 keV per incident electron were deposited inside the pillar apexes by 5 keV and 20 keV electrons, respectively. The 5 keV electrons lose more energy with respect to the 20 keV electrons due to the known $(\rho Z/M)(\ln(E_0)/E_0)$ dependence of the Bethe stopping power and the fact that 20 keV electrons are all scattered out of the pillar volume. The deposited energy in units of energy per deposited atom is obtained by multiplying (4) with $W$ and the standard deviation becomes $\sigma_W = 0.075 W$.

With the knowledge of the deposited energy we can estimate the beam-induced heating at the pillar apex. Using the formalism outlined in [19] for pillars, a maximum temperature <200 °C for a thermal heat conductivity of the deposited material of 0.3 W K$^{-1}$ m$^{-1}$ is predicted. The heat conductivity value was taken for plasma-assisted CVD of low density hydrogenated amorphous carbon [48].

| E0 (keV) | Composition | 1  | 2  | 3  | 4  | 5  |
|---------|-------------|----|----|----|----|----|
| 5 Cu0.1M0.9 | M0.9 = C0.8O1.2F0.08 | 14.56 | 15.42 | 13.70 | 12.10 | 12.73 |
| 20 Cu0.08M0.94 | M0.94 = C0.7O0.3F0.04 | 7.56 | 8.52 | 7.70 | 6.10 | 6.73 |
| l (μm) | 413 | 340 | 360 | 281 | 256 |
| d (nm) | 0.022 | 0.011 | 0.017 | 0.013 | 0.009 |
| E (GPa) | 16 ± 2 | 20 ± 3 | 17 ± 2 | 23 ± 3 | 27 ± 4 |
| f0 (kHz) | 766 | 600 | 729 | 632 | 567 |
| $\rho_d$ (g cm$^{-3}$) | 2.0 ± 0.2 | 2.2 ± 0.2 | 2.3 ± 0.2 | 2.8 ± 0.2 | 2.7 ± 0.2 |
| $\rho_n$ (g cm$^{-3}$) | 1.0 ± 0.1 | 1.2 ± 0.1 | 1.3 ± 0.1 | 2.2 ± 0.2 | 2.1 ± 0.2 |
| Q (→) | 145 ± 44 | 345 ± 104 | 550 ± 165 | 194 ± 58 | 316 ± 95 |
| D (c/atom) | 9.0 ± 0.7 | 11.4 ± 0.9 | 10.7 ± 0.8 | 11.3 ± 0.8 | 13.8 ± 1.0 |
| W (keV/c$^-$) | 3.2 | 3.4 | 3.4 | 2.2 | 2.0 |
| W (keV/atom) | 28.9 ± 2.2 | 36.3 ± 2.7 | 36.4 ± 2.7 | 24.8 ± 1.9 | 27.5 ± 2.1 |
4.2. Chemical composition

From table 1 it is seen that the Cu content was approximately doubled for 20 keV and tripled for 5 keV grown pillars with respect to the stoichiometry of the initially injected molecule. Interestingly, the oxygen content in the deposit is slightly larger than in the original molecule for both energies. This points to the fact that the residual gas, mainly water, inside the microscope chamber contributes to the final composition of the deposit, as was also observed for FEB-induced deposition with nickel-containing molecules [55]. The carbon content in the matrix is 70 at.% for the 20 keV and 60 at.% for the 5 keV pillars. Remarkably, the content of the volatile element fluorine is about a factor of two smaller for the 20 keV compared to the 5 keV. This is consistent with our matrix density measurements in section 4.4 which show a factor of two denser matrix for the 20 keV deposits. Evidently, there is a pronounced dependence in section 4.4 which show a factor of two denser matrix for the 20 keV deposits. Evidently, there is a pronounced dependence on the primary electron energy in the range of 5–20 keV. Within this range of primary electrons, normally all the electronic transitions leading to molecular dissociation (dissociative electron attachment, dissociation into neutrals, dissociative ionization) and the related electron-stimulated desorption are in constant operation. Also, the relatively small dose range of 9–14 electrons/atom does not point to a change in the deposition regime, for instance from electron-limited to precursor-limited. This leads us to propose a sputtering mechanism, which relies on direct momentum transfer, as being responsible for the fluorine reduction. Such a mechanism depends on the primary electron energy: the maximum kinetic energy $E_{\text{max}}$, which can be transferred from an electron with mass $m_e$ and energy $E_0$ in a collision with an atom inside the deposit with mass $m_a$ is [19]

$$E_{\text{max}}(E_0) \cong 4E_0 m_e/m_a.$$  \hspace{1cm} (5)

Maximum transferred energies are summarized for all volatile atoms of Cu(C$_5$H$_{10}$F$_6$O$_2$)$_2$ in table 2. An atom can be sputtered from the surface when the transferred energy is larger than its surface binding energy. The corresponding sputter rate can be found in [56]. Typical displacement energies for polymers were categorized to be within 2–5 eV depending on bond strength, atomic network and atomic weight of constituent atoms. Due to the reduced atomic network, surface binding energies are somewhat smaller than displacement energies.

From table 2 it is evident that a 5 keV electron can transfer only to hydrogen energy of >2 eV necessary for sputtering. At 20 keV, however, fluorine can in principle be displaced or sputtered when accepting 2 eV as a lower limit for the threshold (displacement or sputter) energy.

| $E_0$ (keV) | H | O | F |
|------------|---|---|---|
| 5          | 10.9 | 0.67 | 0.57 |
| 20         | 44.1 | 2.75 | 2.3 |

4.3. Young’s modulus

The error in the determination of Young’s modulus using (1) and (3) is estimated by taking into account the measurement accuracy and precision of the deposit geometry using the SEM and the calibration of the SiO$_2$ reference cantilever used as the force sensor. Since the pillar dimensions as well as the SiO$_2$ cantilever dimensions are read out from the same SEM, the systematic error of 3% originating from its calibration [57] partly cancels out for the displacement measurements in the deflection test. The maximum systematic error in the determination of Young’s moduli becomes $\Delta E/E = \pm 19\%$. Furthermore, the statistical precision of the pillar length and diameter measured from an SEM image is estimated to 2% due to edge effects. This source leads to a standard deviation $\sigma_E = 0.14E$ in this method.

In figure 7(a) Young’s moduli of deposits from Cu(C$_5$H$_{10}$F$_6$O$_2$)$_2$ are plotted versus the dose. For comparison, Young’s modulus of pure copper is of the order of 130 GPa, while for hydrogenated amorphous carbon (a-C:H) values between 10 and 140 GPa can be found [58]. For our pillar deposits a smaller range of 15–30 GPa is found. Within the statistical measurement error no conclusion can be drawn whether for a given constant primary energy deposit stiffness is driven by deposited energy or dose. However, a more pronounced dependence of stiffness on dose for all deposits can be observed; the energy dependence shows a large scatter in data (see table 1). It is clear that deposits obtained from 20 keV show about 30% higher stiffness than deposits from 5 keV impinging electrons. This is in contrast to measurements on FEB pillar deposits from the precursor phenanthrene (C$_{14}$H$_{10}$); Young’s modulus of these deposits decreased by roughly a factor of two by increasing the acceleration voltage from 5 to 20 kV [29]. In a nanoindentation study on FEB thin film deposits from the precursor paraffin (C$_{22}$H$_{46}$, C$_{24}$H$_{50}$), the Young’s modulus increased by a factor of two with increasing acceleration voltage from 3 to 20 kV [2].
In figure 7(b) our results are compared to Young’s moduli of FEB-deposited materials found in the literature. If the results of differing molecules are to be compared with each other, the total error of 33% = 19% + 14% (systematic error + standard deviation) must be considered, since experiments were performed in different microscopes. The systematic error is not important when data points were collected in the same microscope and compared relative to each other, as in figure 7(a). Note that in figure 7(b) several data points for the same precursor molecule represent measurements on materials deposited with varying conditions, e.g. acceleration voltage, beam current and molecule supply rate. However, due to missing reported data we cannot compare this data in terms of deposited dose or energy.

4.4. Density

The analytical solution for the density of a cylindrical pillar shape with perfectly uniform diameter is found by combining (1) and (2):

$$\rho_m = 0.133 \frac{k_4}{I d^2 f_0},$$

where the pillar’s force constant \(k_4\) is known from the bending tests (see section 3.2) and the pillar’s resonance frequency \(f_0\) from vibration tests (see section 3.3). The analysis of (6) results in a maximum systematic error of the method of the order of \(\sigma_{\rho_m}\) (g cm\(^{-3}\)) \(\pm 13\%\) while the standard deviation is found to be \(\sigma_{\rho_m} = 0.08 \rho_0\) assuming the same SEM measurement accuracies as for the error analysis of the Young’s modulus. The determination of the resonance frequency leads to a negligible error. A rough indication of the high precision in the frequency measurement is given by the low uncertainty to determine the resonance peak maximum, given that the measured quality factors correspond to peaks with typical FWHM of the order of \(10^{-3} f_0\). For comparison, from mass sensing experiments using a piezoresistive cantilever mass sensor integrated into the SEM, the density of FEB deposits could be determined with a maximum error of the order of only 10% which is due to a mass sensor calibration procedure which does not rely on the material properties of the cantilever [60].

Density determination of the non-uniform diameter pillars of figure 1 was performed using FE simulations as described in section 3.4. Table 1 shows that pillars grown at 5 kV have an average density of 2.2 g cm\(^{-3}\) while the pillars grown at 20 kV have a density of 2.8 g cm\(^{-3}\). Interestingly, this increase in the 20 kV deposit density is due to a considerable increase in matrix density and not at all due to the content of dense Cu (\(\rho_{Cu} = 8.96\) g cm\(^{-3}\)) which is, in fact, less than in the 5 kV deposit. The matrix density is calculated by \(\rho_m = (\rho_0 - x \rho_{Cu})/(1 - x)\), where \(x\) is the molar copper content in the pseudo-binary compound Cu\(_x\)M\(_{1-x}\). We found an average matrix density \(\rho_m = 2.2\) g cm\(^{-3}\) for the 20 kV pillars which is almost twice as high as the matrix density \(\rho_m = 1.2\) g cm\(^{-3}\) for the 5 kV pillars.

As for the Young’s moduli, the density show a more pronounced dependence on electron dose than on deposited energy as seen in figure 8(a). Additionally, for the matrix density a dependence on the energy of the primary electrons is seen. This can be related to the sputter mechanism discussed in section 4.2 which needs a high primary electron energy to transfer an energy to the volatile atoms higher than the displacement/surface binding energy. A matrix with less volatile atoms will then better reticulate due to the remaining non-volatile, highly reactive radicals and give a higher density. Evidently, reticulation also has a dose dependence for a given energy of primary electrons as was shown in our previous studies on materials grown with similar conditions and doses from the precursor (hfa)CuVTMS where the deposit density was measured using a cantilever-based mass sensor [45]. The matrix density of 25 kV pillar deposits was found to be of the order of 1 g cm\(^{-3}\), increasing to 2.3–2.45 g cm\(^{-3}\) for an irradiation dose of 9–11 and 15–22 electrons per deposited atom, respectively. The (matrix) density values in figure 8(a) show the same increasing trend towards higher doses and similar absolute values.

Figure 8(b) compares matrix densities of differing molecules. Matrix densities are typically lower than diamond and graphite since the deposited amorphous carbonaceous matrix contains oxygen, hydrogen and fluorine according to the elemental composition of molecules used. The matrix densities...
better compare to strongly hydrogenated amorphous carbon materials.

4.5. Dissipation

From the phase relation at resonance the quality factors $Q$ of the pillars were measured to be of the order of 150–600 at room temperature in vacuum (see figure 9). To our knowledge, these are the first investigations concerning dissipation in FEB-deposited pillars.

The quality factor quantifies the intrinsic energy dissipation in the vibrating structure and the dissipation to the environment [61]. The latter can be neglected in SEM vacuum conditions (background pressure < $10^{-4}$ mbar) and thus $Q$ describes intrinsic losses, acoustic losses in the clamping interface [62–64] and surface losses [65–68]. The phase variation at resonance was used to determine the quality factor of the Cu(C$_5$HF$_6$O$_2$)$_2$ pillars. Successive measurements from several spectra resulted in values that varied up to 30% for the same pillar which we suspect to be within the statistical scatter in the measurement method.

It is known that quality factors of single-crystal nanostructures strongly depend on the sample volume-to-surface ratio which suggests that surface losses dominate dissipation with shrinking resonator dimensions [69, 61, 70]. Due to the low variation of the surface-volume ratio of the investigated pillars this relation could not be confirmed from our data. Figure 9 suggests, however, that the $Q$ of the pillars is related to the deposited energy per deposited atom. The higher energy dose means basically that the temperature at the growing tip apex was hotter which might accelerate reticulation reactions and polymerization, leading in turn to a better homogenized material which dissipates less energy by the above-mentioned mechanisms. Of course, such a ‘homogenization’ can be accomplished also by increasing the electron dose, in the sense of completing such reactions by more electrons.

5. Conclusions

We determined the Young’s modulus, density and quality factors of individual high aspect ratio FEB-deposited pillars using SEM integrated force–deflection and vibration measurements in addition to finite element analysis in order to account for the diameter variations of the pillars. We proposed a sputter mechanism to explain the lower fluorine content and the higher matrix density of the pillars deposited at 20 keV with respect to pillars deposited at 5 keV. At 20 keV all volatile atoms can be sputtered and displaced inside the carbon matrix which leads to a better reticulation and higher density. Besides the dependence on primary electron energy, an additional dependence on electron dose was found for the elastic modulus and the density for a given energy. The first quality factor measurements on such pillars favour a dependence on deposited energy. This energy was calculated via Monte Carlo simulations of electron trajectories and is a measure for the temperature in the pillar apex. Higher temperatures can increase reticulation reactions and homogenize the deposit.

Acknowledgments

We thank Dr Samuel Hoffmann, EMPA, and Fredrik Östlund, EMPA, for the programming of the image processing software. Financial support is acknowledged from the EU project NanoHand.
References

[1] Burbridge D J, Crampin S, Viau G and Gordeev S N 2008 Strategies for the immobilization of nanoparticles using electron beam induced deposition Nanotechnology 19 445302

[2] Ding W, Dikin D A, Chen X, Piner R D, Ruoff R S, Zussman E, Wang X and Li X 2005 Mechanics of hydrogenated amorphous carbon deposits from electron-beam-induced deposition of a paraffin precursor J. Appl. Phys. 98 014905

[3] Utke I, Friedli V, Fahlibusch S, Hoffmann S, Hoffmann P and Michler J 2006 Tensile strengths of metal-containing joints fabricated by focused electron beam induced deposition Adv. Eng. Mater. 8 155–7

[4] Yu M F, Lourie O, Dyer M J, Moloni K, Kelly T F and Ruoff R S 2000 Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load Science 287 637–40

[5] Molhave K, Madsen D N, Dohn S and Boggild P 2004 Constructing, connecting and soldering nanostructures by environmental electron beam deposition Nanotechnology 15 1047–53

[6] Utke I, Hoffmann P, Berger R and Scandella L 2002 High-resolution magnetic Co superlattices grown by a focused electron beam Appl. Phys. Lett. 80 4792–4

[7] Edinger K, Gotszalk T and Rangelow I W 2001 Novel high resolution scanning thermal probe J. Vac. Sci. Technol. B 19 2856–60

[8] Castagne M, Benfedda M, Lahimer S, Falgayrettes P and Fillard J P 1999 Near field optical behaviour of C superlips Ultramicroscopy 76 187–94

[9] Sqalli O, Utke I, Hoffmann P and Marquis-Weible F 2002 Gold elliptical annulomes as probes for near field optical microscopy J. Appl. Phys. 92 1078–83

[10] Akama Y, Nishimura E, Sakai A and Murakami H 1990 New scanning tunneling microscopy tip for measuring surface-topography J. Vac. Sci. Technol. A 8 429–33

[11] Hubner B, Koops H W P, Pagnia H, Sotnik N, Urban J and Weber M 1992 Tips for scanning tunneling microscopy produced by electron-beam-induced deposition Ultramicroscopy 42 1519–25

[12] Matsui S, Baba M and Sato A 1992 Atomic layer etching and sidewall roughness measurement using the scanning tunnelling microscope Nanotechnology 3 156–60

[13] Boggild P, Hansen T M, Tanasa C and Grey F 2001 Fabrication and actuation of customized nanoeoezeters with a 25 nm gap Nanotechnology 12 331–5

[14] Wendel M, Lorenz H and Kothaus J P 1995 Sharpened electron beam deposited tips for high resolution atomic force microscope lithography and imaging Appl. Phys. Lett. 67 3732–4

[15] Kometani R, Hoshino T, Kondo K, Kanda K, Haruyama Y, Kaito T, Fujita J, Ishida M, Ochiai Y and Matsui S 2005 Performance of nanomanipulator fabricated on glass microscope tethering and imaging J. Appl. Phys. 1

[16] Kometani R, Kakei H, Kanda K, Haruyama Y, Kaito T and Matsui S 2007 Fabrication of a focused ion-beam chemical vapor deposition and actuation of nanomanipulator J. Vac. Sci. Technol. B 23 298–301

[17] van Dorp W F, van Someren B, Hagen C W and Kruit P 2005 Approaching the resolution limit of nanometer-scale electron beam-induced deposition Nano Lett. 5 1303–7

[18] Fujita J, Ishida M, Ichihashi T, Ochiai Y, Kaito T and Matsui S 2003 Carbon nanopillar laterally grown with electron beam-induced chemical vapor deposition J. Vac. Sci. Technol. B 21 2990–3

[19] Utke I, Hoffmann P and Melngailis J 2008 Gas-assisted electron beam and ion beam processing and fabrication J. Vac. Sci. Technol. B 26 1197–276

[20] Prorok B, Zhu Y, Espinosa H, Guo Z, Bazant Z, Zhao Y and Yakobson B 2004 Encyclopedia of Nanoscience and Nanotechnology vol 5, ed Nalwa (Stevenson Ranch, CA: American Scientific Publishers) pp 555–600

[21] Friedli V, Hoffmann S, Michler J and Utke I et al 2008 Applied Scanning Probe Methods VIII ed B Bhushan (Heidelberg: Springer) pp 247–88

[22] Fujita J, Ishida M, Ichihashi T, Ochiai Y, Kaito T and Matsui S 2003 Growth of three-dimensional nano-structures using FIB-CVD and its mechanical properties Nucl. Instrum. Methods Phys. Res. B 206 472–7

[23] Fujita J, Ishida M, Sakamoto T, Ochiai Y, Kaito T and Matsui S 2001 Observation and characteristics of mechanical vibration in three-dimensional nanostructures and pillars grown by focused ion beam chemical vapor deposition J. Vac. Sci. Technol. B 19 2834–7

[24] Fujita J, Okada S, Ueki R, Ishida M, Kaito T and Matsui S 2007 Elastic double structure of amorphous carbon pillar grown by focused-ion-beam chemical vapor deposition Japan. J. Appl. Phys. 46 6286–9

[25] Ishida M, Fujita J, Ichihashi T, Ochiai Y, Kaito T and Matsui S 2003 Focused ion beam-induced fabrication of tungsten structures J. Vac. Sci. Technol. B 21 2728–31

[26] Ishida M, Fujita J and Ochiai Y 2002 Density estimation for amorphous carbon nanopolars grown by focused ion beam assisted chemical vapor deposition J. Vac. Sci. Technol. B 20 2784–7

[27] Nakamatsu K, Nagase M, Iyki I Y, Namatsu H and Matsui S 2005 Mechanical characteristics and its annealing effect of diamondlike-carbon nanosprays fabricated by focused-ion-beam chemical vapor deposition J. Vac. Sci. Technol. B 23 2801–5

[28] Okada S, Mukawa T, Kobayashi R, Fujita J, Ishida M, Ichihashi T, Ochiai Y, Kaito T and Matsui S 2005 Growth manner and mechanical characteristics of amorphous carbon nanopolars grown by electron-beam-induced chemical vapor deposition Japan. J. Appl. Phys. 1

[29] Okada S, Mukawa T, Kobayashi R, Ishida M, Ochiai Y, Kaito T, Matsui S and Fujita J 2006 Comparison of Young’s modulus dependence on beam accelerating voltage between electron-beam- and focused-ion-beam-induced chemical vapor deposition pillars J. Appl. Phys. 1

[30] Janchen G, Hoffmann P, Kriete A, Lorenz H, Kulik A J and Dietler G 2002 Mechanical properties of high-aspect-ratio atomic-force microscope tips Appl. Phys. Lett. 80 4623–5

[31] Young W C and Budyans R G 2002 Roark’s Formulas for Stress and Strain (New York: McGraw-Hill)

[32] Weaver W, Timoshenko S P and Young D H 1990 Vibration Problems in Engineering (New York: Wiley)

[33] Timoshenko S P, Young D H and Weaver W 1974 Vibration Problems in Engineering (New York: Wiley)

[34] Nonaka K, Tamura K, Nagase M, Yamaguchi H, Warisawa S and Ishihara S 2008 Modulus Young’s modulus for carbon nanopolars grown by focused-ion-beam-induced chemical vapor deposition Japan. J. Appl. Phys. 27 45556–9

[35] Friedli V and Utke I 2009 Optimized molecule supply from nozzle-based gas injection systems for focused electron and ion-beam-induced deposition and etching: simulation and experiment J. Phys. D: Appl. Phys. 42 125305

[36] Mitsuishi K, Shimoji M, Takeguchi M, Tanaka M and Furuya K 2006 Proximity effect in electron-beam-induced deposition Japan. J. Appl. Phys. 45 5517–21

[37] Utke I, Bret T, Laba D, Buffat P, Scandella L and Hoffmann P 2004 Thermal effects during focused electron beam induced deposition of nanocomposite magnetic–cobalt-containing tips Microelectron. Eng. 73/74 553–8
[38] Molhave K, Madsen D N, Rasmussen A M, Carlsson A, Appel C C, Bronson M, Jacobsen C J H and Boggild P 2003 Solid gold nanostructures fabricated by electron beam deposition Nano Lett. 3 1499–503
[39] Rack P D 2007 In situ probing of the growth and morphology in electron-beam-induced deposited nanostructures Nanotechnology 18 465602
[40] Gibson C T, Watson G S and Myhra S 1997 Scanning force microscopy—calibrative procedures for ‘best practice’ Scanning 19 564–81
[41] Jaccodin Rj and Schlegel W A 1966 Measurement of strains at Si–SiO2 interface J. Appl. Phys. 37 2429
[42] Hoffmann S, Utke I, Moser B, Michler J, Christiansen S H, Schmidt V, Senz S, Werner P, Gossele U and Ballif C 2006 Measurement of the bending strength of vapor–liquid–solid grown silicon nanowires Nano Lett. 6 622–5
[43] Perisanu S, Vincent P, Ayari A, Choueib M, Guillot D, Bechelany M, Corru D, Miele P and Purcell S T 2007 Ultra high sensitive detection of mechanical resonances of nanowires by field emission microscopy Phys. Status Solidi a 204 1645–52
[44] Calabri L, Pugno N, Ding W and Ruoff R S 2006 Resonance of curved nanowires J. Phys.: Condens. Matter 18 S2175–83
[45] Utke I, Friedli V, Michler J, Bret T, Multone X and Hoffmann P 2006 Density determination of focused-electron-beam-induced deposits with simple cantilever-based method Appl. Phys. Lett. 88 031906
[46] Bret T, Mauron S, Utke I and Hoffmann P 2005 Characterization of focused electron beam induced carbon deposits from organic precursors Microelectron. Eng. 78/79 300–6
[47] Reimer L 1998 Scanning Electron Microscopy Physics of Image Formation and Microanalysis (Berlin: Springer)
[48] Bullen A J, O’Hara K E, Cahill D G, Monteiro O and von Keudell A 2000 Thermal conductivity of amorphous carbon thin films J. Appl. Phys. 88 6317–20
[49] Kodas T T and Hampden-Smith M J 1994 The Chemistry of Metal CVD (Weinheim: VCH)
[50] van Dorp W F and Hagen C W 2008 A critical literature review of focused electron beam induced deposition J. Appl. Phys. 104 081301
[51] Randolph S J, Fowlkes J D and Rack P D 2005 Effects of heat generation during electron-beam-induced deposition of nanostructures J. Appl. Phys. 97 124312
[52] Utke I, Michler J, Gasser P, Santschi C, Laub D, Cantoni M, Buffat P A, Jiao C and Hoffmann P 2005 Cross section investigations of compositions and sub-structures of tips obtained by focused electron beam induced deposition Adv. Eng. Mater. 7 323–31
[53] Hochleitner G, Wanzenboeck H D and Bertagnolli E 2008 Electron beam induced deposition of iron nanostructures J. Vac. Sci. Technol. B 26 939–44
[54] Utke I, Luisier A, Hoffmann P, Laub D and Buffat P A 2002Focused-electron-beam-induced deposition of freestanding three-dimensional nanostructures of pure coalesced copper crystals Appl. Phys. Lett. 81 3245–7
[55] Perentes A, Sinicco G, Boero G, Dwir B and Hoffmann P 2007Focused electron beam induced deposition of nickel J. Vac. Sci. Technol. B 25 2228–32
[56] Egerton R F, Li P and Malac M 2004 Radiation damage in the TEM and SEM Microsc. 35 399–409
[57] Hitachi High-Technologies Corp. 2008 personal communication
[58] Robertson J 2002 Diamond-like amorphous carbon Mater. Sci. Eng. R 37 129–281
[59] Wich T, Kray S and Fatikow S 2006 Microrobot-based testing of nanostructures inside an SEM Actuator ed H Borgmann (Bremen, Germany: Messe Bremen) pp 382–5
[60] Friedli V, Santschi C, Michler J, Hoffmann P and Utke I 2007 Mass sensor for in situ monitoring of focused ion and electron beam induced processes Appl. Phys. Lett. 90 053106
[61] Ekinci K L and Roukes M L 2005 Nanoelectromechanical systems Rev. Sci. Instrum. 76 061101
[62] Cross M C and Lifshitz R 2001 Elastic wave transmission at an abrupt junction in a thin plate with application to heat transport and vibrations in mesoscopic systems Phys. Rev. B 64 085324
[63] Jiang H, Yu M F, Liu B and Huang Y 2004 Intrinsic energy loss mechanisms in a cantilevered carbon nanotube beam oscillator Phys. Rev. Lett. 93 185501
[64] Photiadis D M and Judge J A 2004 Attachment losses of high Q oscillators Appl. Phys. Lett. 85 482–4
[65] Wang Y, Henry J A, Zehnder A T and Hines M A 2003 Surface chemical control of mechanical energy losses in micromachined silicon structures J. Phys. Chem. B 107 14270–7
[66] Yang J L, Ono T and Esashi M 2000 Surface effects and high quality factors in ultrathin single-crystal silicon cantilevers Appl. Phys. Lett. 77 3860–2
[67] Yang J L, Ono T and Esashi M 2001 Investigating surface stress: surface loss in ultrathin single-crystal silicon cantilevers J. Vac. Sci. Technol. B 19 551–6
[68] Yasumura K Y, Stowe T D, Chow E M, Pfäffman T, Kenny T W, Stipe B C and Rugar D 2000 Quality factors in micron- and submicron-thick cantilevers J. Phys. Chem. B 104 5169–521
[69] Carr D W, Evoy S, Sekaric L, Craigehead H G and Parpia J M 1999 Measurement of mechanical resonance and losses in nanometer scale silicon wires Appl. Phys. Lett. 75 920–2
[70] Perisanu S, Vincent P, Ayari A, Choueib M, Purcell S T, Bechelany M and Corru D 2007 High Q factor for mechanical resonances of batch-fabricated SiC nanowires Appl. Phys. Lett. 90 043113