Perpendicular Iron Nanopillars by Electron Beam Induced Deposition

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Introduction

Focused electron beam induced deposition (FEBID) is a versatile maskless method for direct fabrication of nanoscaled structures. This method allows the direct deposition of material on every surface. In contrast to conventional lithography, FEBIP is capable of fabricating 3-dimensional structures with complex geometry, which has been demonstrated by Matsui et al [1]. The method relies on the chemical vapor deposition (CVD) induced by impinging electrons from a focused beam. Using a focused electron beam FEBID allows a spatial resolution below 2 nm when using a TEM [2]

For deposition volatile metal precursors containing metalorganic compounds such as acetylacetonates [3], inorganic compounds such as trifluorophosphine metal compound and metal carbonyls [4] have been demonstrated. Due to the simplicity of the molecular structure of the complex and of the ligand metal, carbonyls of the type $Me(CO)_n$ are especially suited for study of the mechanism, and FEBID of Co, Fe, Ni, Cr, Ru has already been performed [5]. The adsorption of $Fe(CO)_5$ was studied by Cheng *et al.* [6]; also autocatalytic growth was observed [13]. Although deposition processes have been widely applied the underlying reaction mechanisms remained unclear. The *in-situ* nano-deposition of electrically conductive and of magnetic materials has been of increasing research interest, and FEBID was used to contact carbon nanotubes [7], to fabricate Hall sensors, and to generate magnetic structures [8].

This paper reports the observation of a slow vertical growth regime and a fast radial growth regime. The conditions under which these growth regimes occur and influence parameters are reported. A comparison with mechanisms proposed by literature is performed.

Experimental

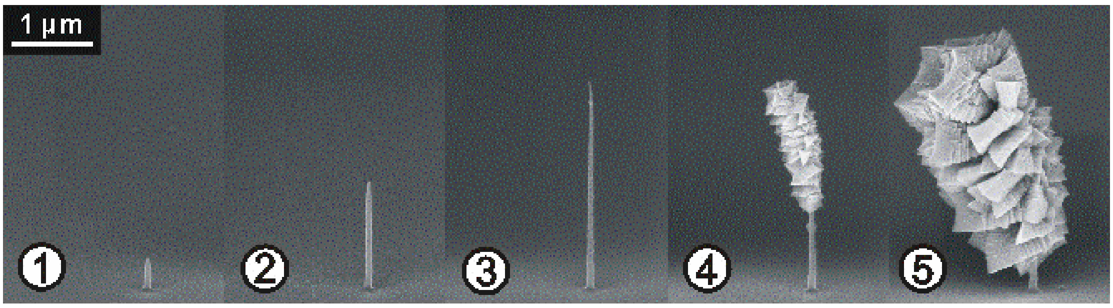
As substrate silicon with a native oxide layer was used. The iron carbonyl (CAS: [13463-40-6]) was used without further purification. The actual beam current was measured before deposition using a faraday cup. The deposition setup is based on a ZEISS Leo 1530VP electron microscope with a Schottky-emitter operated at 1 to 20 keV acceleration voltage. A base pressure of 1.4E-6 mbar was achieved with an oil-free pumping system. The precursor was provided by a custom-tailored gas injection system made of steel featuring an external reservoir, a dosing valve, a vacuum gauge to measure the precursor pressure in the supply line ("pre-chamber-pressure"), and a motorized nozzle head with 3 gas nozzles made of glass tubes with an inner diameter of 600 nm. The final position of the nozzle was adjusted to be 300 nm above the sample surface and in a 500 nm distance from the deposition area.

The probe current was monitored with a 1 s time resolution as current flux from the electrically isolated sample holder. For chemical and structural studies the sample had to be removed from the Leo 1530 VP and was exposed to ambient environment. Analysis was performed without further sample preparation and without thermal processing. The chemical composition was measured by X-ray emission spectroscopy (EDX) in a Philips XL30 electron microscope (equipped with a rotary pump).

Results

Depositions were performed in the spot mode of the electron microscope in order to avoid effects caused by the beam scan parameters. Simultaneously to all depositions the electrical current flowing from the deposition area (”specimen current”) was measured. The specimen current results from the incoming electrons of the primary beam and the outgoing electrons comprising emitted secondary electrons, backscattered electrons and Auger electrons. For an 10 keV electron beam in Si a scattering of the primary electrons over a depth of 1.3 µm and a diameter up to 2 µm has been calculated. With the deposition of pillars it has to be considered that the interaction volume of the electron beam may be larger than the dimensions of the deposited pillar. Hence, the portion of outgoing electrons will vary not only with the chosen acceleration energy of the primary electrons but also with the geometry of the deposited pillar.

During the deposition of iron pillars two different growth regimes were observed. Typical representatives of this growth process are depicted in Fig. 1. The vertical growth regime is characterized by no further radial growth occurring during ongoing length growth of the pillar. After a short tip-forming phase a constant vertical growth rate was observed for the first 45 seconds of growth time – at longer times the vertical growth rates slightly decreased as a result of a changing tip geometry. For a 1.97 nA electron beam with 10 keV and a 0.5 mbar $Fe(CO)_5$ precursor pressure in the supply line, which is equivalent to a chamber pressure of ~1E-5 mbar, vertical growth rate was in the range of 48 nm/s. The full width at half maximum of the pillars was in the range of 70 nm (+/- 5 nm) and was roughly constant over the entire length of the pillar. The constant vertical growth rate is also displayed by positive specimen current (Fig. 2) that is constant during the initial 45 seconds. Between 45 seconds and 65 seconds the broad tip cone transformed into a sharper cone, which slightly increased the specimen current. The positive specimen current indicates that more electrons (secondary electrons, backscattered electrons) are emitted than primary electrons from the focused beam are arriving at the sample. The current during the first 5 – 7 seconds is attributed to a tip-forming phase and is not representative.



(a) (b) (c) (d) (e)

Fig. 1: Free-standing pillars deposited from $Fe(CO)_5$ with a 10 keV 1.97 nA focused electron beam. The $Fe(CO)_5$ in the supply line was 0.5 mbar resulting in a 1.0x10E-5 mbar chamber pressure. The depositions are depicted by SEM at a 75° tilt after a deposition time of (a) 10 s, (b) 30 s, (c) 60s , (d) 75 s and (e) 110s

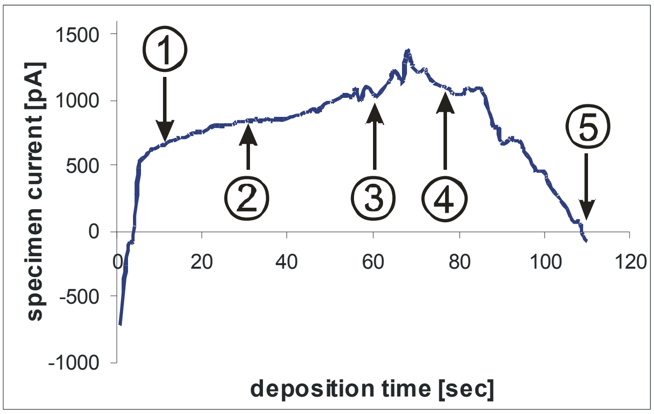
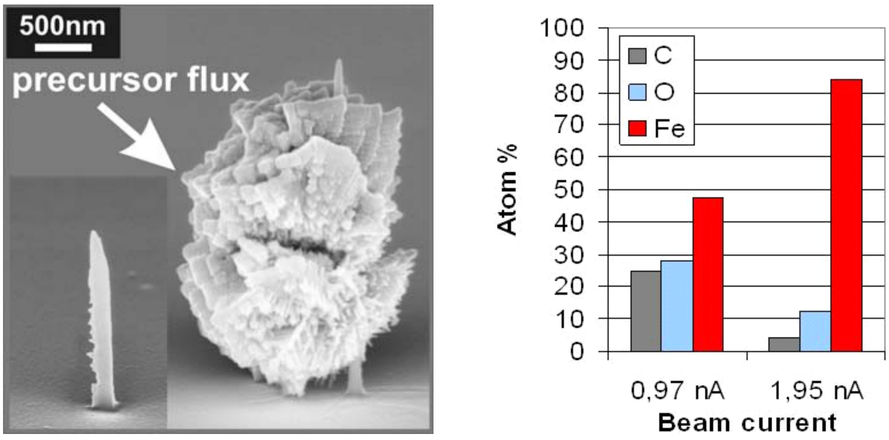


Fig. 2: Specimen current (current flowing off from the deposition area) monitored with progressing deposition time. The metal deposition was performed with a 10 keV 1.97 nA focused electron beam with a supply line pressure of 0.5 mbar $Fe(CO)_5$. This current monitoring graph relates to Fig. 1.

The radial growth regime is characterized by a fast radial growth of dendritic structures quickly increasing the diameter of the pillar. In comparison to the preceding vertical growth regime, in radial growth regime the height growth rate is significantly reduced. For a 1.97 nA electron beam with 10 keV and a 0.5 mbar precursor pressure in the supply line vertical growth rate was quenched to 15 nm/s while a radial growth rate of 19 nm/s was observed. The radial growth resulting in a strongly increased pillar diameter is also displayed as reversion of the specimen current towards negative values (Fig. 2). This change of the specimen current (Fig. 2) reproducibly occurred after 70 seconds deposition time. The negative slope of the specimen current during radial growth indicates that increasingly fewer electrons are emitted from the pillar structure. As the steadily decreasing specimen current was observed simultaneously with a growing diameter of the pillar, it is assumed that the larger volume of the pillar prevents more electrons from reaching the surface and reduces emission. The radial growth sets in autonomously and reproducibly starts at the tip of the slim pillar, but also progresses towards the bottom of the stem (Fig. 1). The self-sustained growth downward the stem supports the assumption of autocatalytic effects. That the radial growth reproducibly starts at the same pillar height may be explained by thermal heating of the pillar by the electron beam. Due to the low thermal conductivity of the slim pillar a thermal heating of the tip has been suggested by Utke *et al*. [9].

The effect of the beam current on the growth rate during the vertical growth regime was investigated with two different experiments. First different apertures with a 10 keV beam were used. Smaller apertures with a lower beam current resulted in a slower growth rate. With a 10 µm aperture (57 pA) as well as a 20 µm aperture (209 pA) no radial growth was observed during the deposition time up to 360 seconds although nanopillar heights up to 5.3 µm were achieved. This behavior supports the assumption of thermal effects as the thermal conduction of the wire may be sufficient to avoid high tip temperatures with the smaller beam currents. Radial growth never occurred with beam currents below 500 nA but was observed reproducibly with higher beam currents.

Alternatively the operation mode of the Zeiss 1530 VP was switched between “normal current” and “high current” which facilitates to change the beam current without changing the acceleration voltage or the aperture setting. For a 10 keV beam and a 60 µm aperture a beam current of either 0.97 nA (normal current mode) or alternatively 1.96 nA (high current mode) could be provided. After the same deposition time of 240 s (Fig. 3) with the 0.97 nA beam no radial growth of the 2.5 µm high pillar was observed, while with the stronger 1.97 nA beam radial growth of the 4.76 µm high pillar occurred.



(a) (b) (c)

Fig. 3: Iron deposition at 10 kV with a 60 µm aperture after 240 s (left) in low current mode 0.97 nA and (b) in high current mode 1.97 nA (image is 75° tilted) and chemical composition of these structures as determined by x-ray emission spectroscopy

The chemical composition of the deposited structures of Fig. 3(a) and Fig. 3(b) was measured by EDX (Fig. 3(c)). For transfer to the EDX tool samples were exposed to ambient conditions. For the slim pillar deposited solely in the vertical growth regime the Fe content was 48% while 28% oxygen and 24% carbon were significant impurities. With the broad pillar mainly deposited in a self-sustained radial growth regime an 84% Fe content was measured while contaminants were strongly decreased to 10% oxygen and 6% carbon. This result suggests that material grown in the radial growth mode has a higher iron purity.

Conclusion

The deposition of iron nanopillars by focused electron beam induced deposition from iron pentacarbonyl was demonstrated. Two different growth regimes were observed. Within the vertical growth regime slim pillars with height growth rates between 25 and 55 nm/s were obtained. Within the radial growth regime fast lateral growth of dendritic structures with a low contamination level (below 20%) was observed.

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