Annealing-Based Electrical Tuning of Cobalt−Carbon Deposits Grown by Focused-Electron-Beam-Induced Deposition

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In this work we present an effective postgrowth electrical tuning, via oxygen releasing method, to enhance the content of non-noble metals in deposits directly written with gas-assisted focused-electron-beam-induced deposition (FEBID). It represents a novel and reproducible method for improving the electrical transport properties of Co−C deposits.[1,2] The metal content and electrical properties of Co−C−O nanodeposits obtained by electron-induced dissociation of volatile $Co_2(CO)_8$ precursor adsorbate molecules were reproducibly tuned by applying postgrowth annealing processes at 100 °C, 200 °C, and 300 °C under pressures below 5×10^{-5} mbar for 10 min. Advanced thin film EDX analysis showed that during the annealing process predominantly oxygen is released from the Co−C−O deposits, yielding an atomic ratio of Co:C:O = 100:16:1 (85:14:1) with respect to the atomic composition of as-written Co:C:O = 100:21:28 (67:14:19) (Figure 1a). In-depth Raman analysis (Figure 1b) suggests that the amorphous carbon contained in the as-written deposit turns into graphite nanocrystals with size of about 22.4 nm with annealing temperature. Transmission electron microscopy (TEM) analysis showed reduction of the hexagonal-closed-packed (hcp) Co_3O_4 molecules into metallic face-centered-cubic (fcc)/hcp Co during annealing. Remarkably, these microstructural changes allow for tuning of the electrical resistivity of the deposits over 3 orders of magnitude from 26 mΩ cm down to 26 μΩ cm (Figure 2), achieving a residual resistivity of $\rho_{2\,K}/\rho_{300\,K} = 0.56$ (Figure 3), close to the value of 0.53 for pure Co films with similar dimensions.[3] In addition, the magnetoresistance (MR) signal found in our FEBID granular nanocomposites are about one order of magnitude larger than those found in pure Co with similar dimensions defined by electron beam lithography (EBL), making it especially interesting and advantageous over the numerous works already published for applications such as advanced scanning-probe systems, magnetic memory, storage, and ferroelectric tunnel junction memristors.

[1] Fernández-Pacheco, A., *et al*., 2009, *J. Phys. D: Appl. Phys.* **42**, 055005.
[2] Puydinger dos Santos, M. V., *et al*., 2016, *ACS Appl. Mater. Interfaces* **8**, 32496.
[3] De Vries, J. W. C., 1988, *Thin Solid Films* **167**, 25.

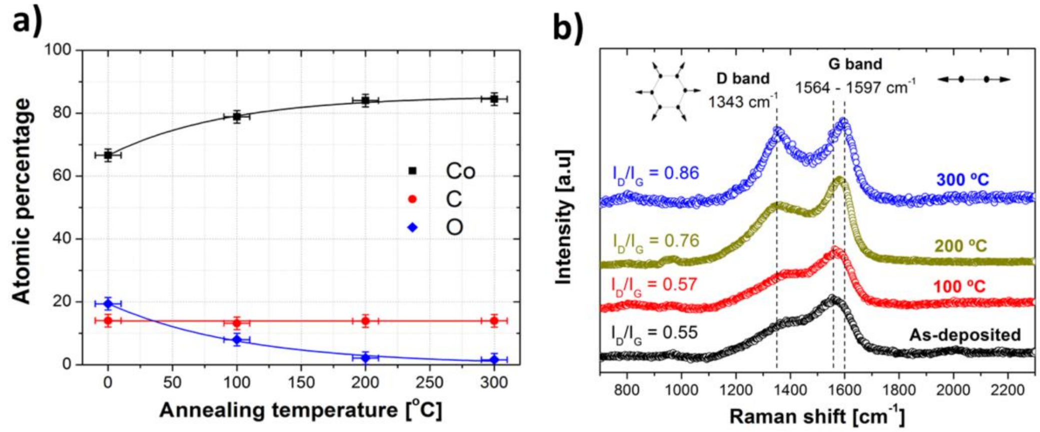

Figure 1: (a) Thin film corrected atomic composition analysis by EDX and (b) Raman spectra in the carbon range (disordered carbon band, D (1350 cm^{-1}), and graphitic band, G (1580 cm^{-1}) are present) as a function of the postgrowth annealing temperature.

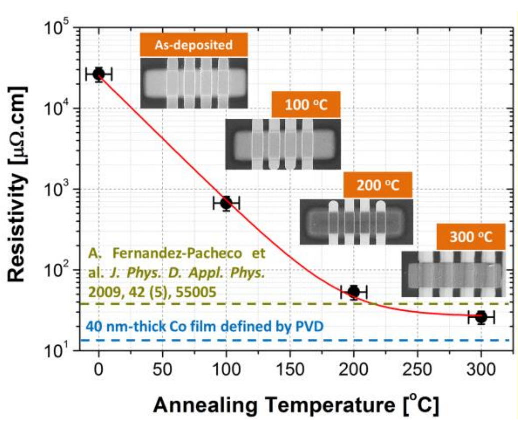

Figure 2: Resistivity of Co FEBID material as a function of postgrowth annealing temperature, measured for five different samples at each temperature. Insets show top view SEM images of the four-point platinum electrodes taken at 3 keV.

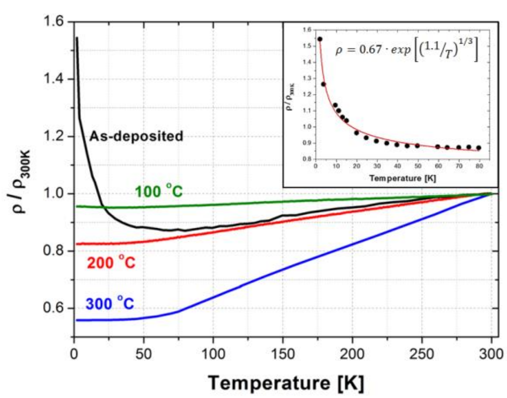

Figure 3: Normalized electrical resistivity of Co-FEBID deposits as a function of the temperature during cooling from 300 K to 2 K of the as-deposited as well as the annealed samples at 100 °C, 200 °C, and 300 °C. *Inset*: Normalized resistivity during the cooling process for the as-deposited Co−C FEBID material. Mott's variable-range hopping mechanism fits our experimental data and gives a bi-dimensional thin film deposit.