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Atomic layer deposition of cobalt carbide films and their magnetic properties using propanol as a reducing agent

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ABSTRACT

The investigation of highly conformal thin films using Atomic Layer Deposition (ALD) is driven by a variety of applications in modern technologies. In particular, the emergence of 3D memory device architectures requires conformal materials with tuneable magnetic properties. Here, nanocomposites of carbon, cobalt and cobalt carbide are deposited by ALD using cobalt acetylacetonate with propanol as a reducing agent. Films were grown by varying the ALD deposition parameters including deposition temperature and propanol exposure time. The morphology, the chemical composition and the crystalline structure of the cobalt carbide film were investigated. Vibrating Sample Magnetometer (VSM) measurements revealed magnetic hysteresis loops with a coercivity reaching 500 Oe and a maximal saturation magnetization of 0.9 T with a grain size less than 15 nm. Magnetic properties are shown to be tuneable by adjusting the deposition parameters that significantly affect the microstructure and the composition of the deposited films.

1. Introduction

Magnetic materials constitute an active field of research that is driven by a variety of applications in biomedicine, ferrofluids, catalysis, and magnetic memory devices [1]. Rare earth based materials [2] have for long been potential candidates to achieve good magnetic properties but the volatility of their prices and their environmental impact have motivated interest toward other alternatives [3]. Certain transition metal carbides have sparked a great interest due to their promising magnetic properties [4]. In particular cobalt and cobalt carbide based materials have been identified for applications requiring a high signal to noise ratio [5] and hard magnetic media because of their high coercivity [6]. The addition of carbon has been established as a means to enhance the magnetic anisotropy of cobalt [7]. A coercivity reaching 3.4 kOe has been demonstrated [7]. The coercivity for “graphite-shell encapsulated cobalt nanofibers” was reported at 261.3 Oe [8]. The coercivity of bulk cobalt was also reported by Wu et al. [9]. Electrodeposited thin cobalt films yield a coercivity ranging from 15 to 380 Oe, depending on the crystallographic structure [9]. Carbon encapsulation prevents oxidation and agglomeration of the magnetic transition metal nanoparticles which preserves their magnetic properties [10,11]. In addition, cobalt and cobalt-based alloys were demonstrated to provide good mechanical, optical [12,13] and catalytic properties [14]. Several techniques have been used to produce cobalt carbide powders [15] and thin films. For thin films, these include chemical vapour deposition (CVD), [16] physical vapour deposition (PVD) [17] and electrochemistry [18]. Compared to these techniques, atomic layer deposition (ALD) presents the advantage of yielding coatings with excellent thickness control. It is particularly attractive for 3D advanced logic devices for which complex structures require conformal coatings [19].

We report here for the first time to our knowledge the ALD of cobalt carbide using cobalt acetylacetonate as precursor and propanol as a reducing agent. The growth of metal or alloy thin films by ALD relies on inorganic, metal-organic or organo-metallic precursors [20]. Metal-organic compounds are readily available and convenient to handle and store. Furthermore, the safety and the availability of propanol have motivated its use as a reducing agent. The ability of propanol to reduce metal acetylacetonate was first demonstrated in the CVD mode [21]. More recently our team

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described the ALD growth [22] of nickel carbide films using alcohols.

Focusing on the magnetic properties of cobalt carbide thin films, this study deals with their highly conformal growth using ALD with a Co(acac)$_2$ precursor and propanol as a reducing agent. The chemical composition, the microstructure and the morphology of the films are investigated. The magnetic properties are studied as a function of the deposition temperature, the film thickness and the propanol exposure time during the deposition cycles.

2. Experimental

The ALD of cobalt carbide was performed on a silicon oxide (SiO_2) layer which was thermally grown on (100) silicon at 1100 °C. The SiO_2 thickness was measured by ellipsometry to be 50 nm, which is sufficiently thick to exclude the formation of silicides [23]. The substrates were ultrasonically cleaned in acetone and in ethanol prior to deposition.

The coatings were made using the as-received cobalt acetylacetonate and propanol (Sigma Aldrich) in a Beneq TFS200 setup. The sublimation hot source was used at 155 °C for cobalt acetylacetonate, while propanol was evaporated at room temperature. The purge of the reactor was ensured with a continuous nitrogen flow of 300 sccm.

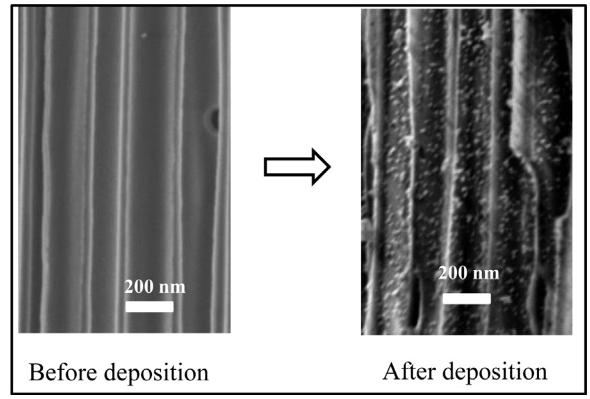

Fig. 1. SEM-micrograph of the fractured cross-section of cobalt carbide nanoparticles deposited on an anodic aluminium oxide membrane using Co(acac)$_2$ and propanol at 350 °C; t_{Co} = 3 s; t_{prop} = 4 s, t_P = 2 s; the reactor pressure was 3 mbar; The deposit corresponds to 1000 deposition cycles.

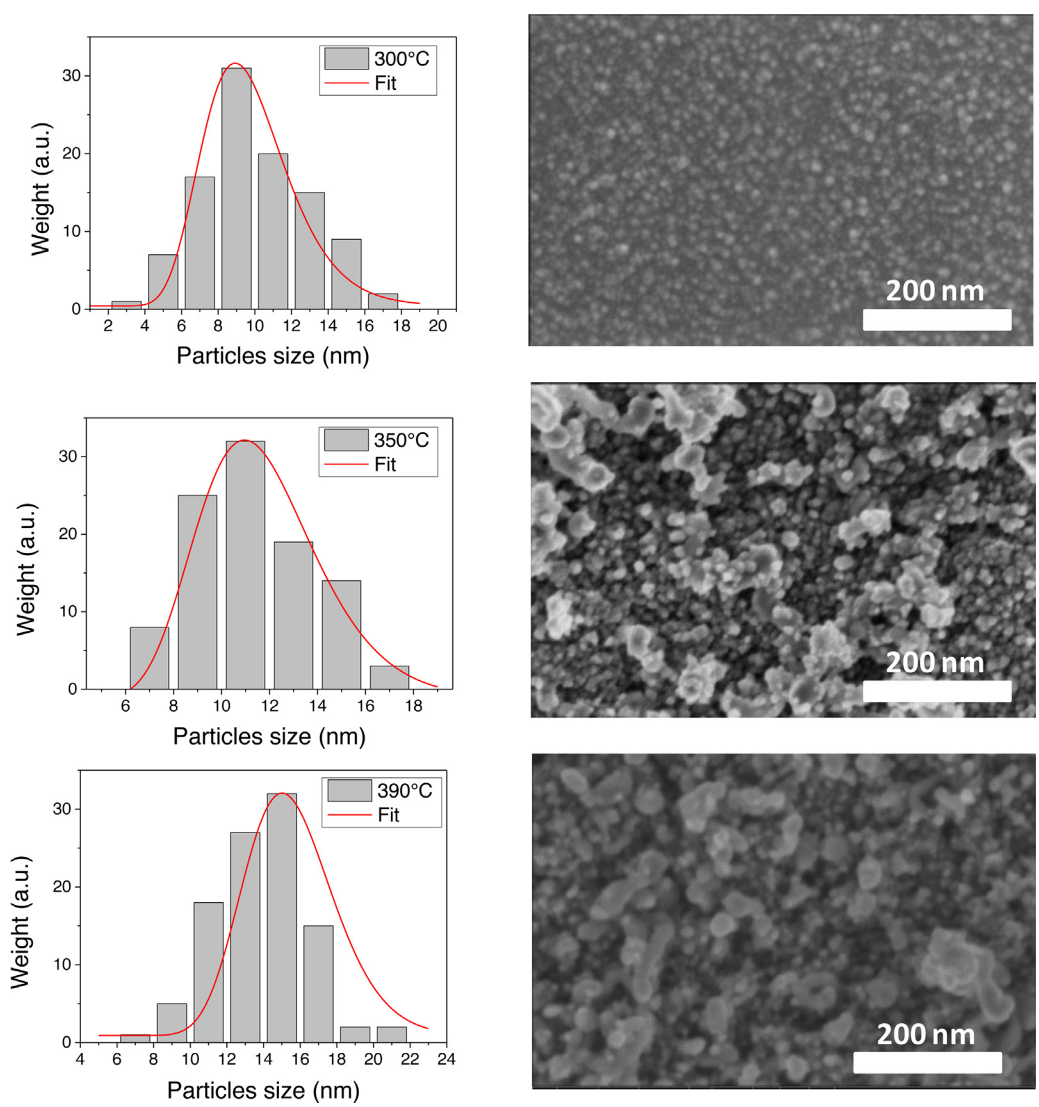

Fig. 2. SEM-micrographs (right) and grain size distribution (left) of films grown at various temperatures; t_{Co} = 3 s, t_{prop} = 4 s, t_P = 2s, the reactor pressure: 3 mbar; the displayed coatings correspond to 3000 deposition cycles.