Chemical vapour deposition of cobalt for magnetic applications

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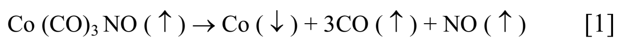
The interest in magnetic thin films has increased rapidly due to the discovery of the giant-magnetoresistance (GMR) effect exhibited by magnetic multilayer structures (1), spin valves and granular alloys for both magnetic and non-magnetic metals. Much of the published work on magnetic thin films has reported the properties of magnetic layers grown by physical deposition techniques such as sputtering, molecular beam epitaxy (MBE) and evaporation. The alternative technique of Chemical Vapour Deposition (CVD) has the ability to coat substrate topographies uniformly with well-controlled thin layers without radiation damage and it may allow selective deposition.

In this work an investigation into the use of CVD as a means of depositing thin magnetic layers of cobalt was conducted. A liquid, cobalt tri-carbonyl nitrosyl ($Co(CO)_3NO$) was used. Depositions on oxidised silicon wafers were then analysed chemically, electrically and magnetically to provide key process parameters and an understanding of the growth kinetics.

A Varian low pressure CVD reactor was re-developed to create a load-locked, single 100mm substrate process chamber using a radiantly heated graphite susceptor. A thermocouple embedded in the graphite susceptor provides temperature feedback. The precursor is maintained at $0^{\circ}C$ in a chilled stainless steel vessel using thermoelectric coolers. This provides a vapour pressure of 25 torr as input to the hydrogen-calibrated 20 sccm MFC delivery system. Nitrogen and hydrogen gas can also be supplied to the process chamber under MFC control. During deposition the precursor gas lines are heated to 50°C and the process chamber walls are allowed to heat up to avoid condensation of the precursor. Only the external tungsten-halogen lamp housing and top-plate are water-cooled. System base pressure was 10^{-2} torr using rootes-rotary pumping.

The desired deposition chemistry utilises the irreversible reaction:



$$Co\,(CO)_3NO\,(\uparrow) \rightarrow Co\,(\downarrow) + 3CO\,(\uparrow) + NO\,(\uparrow) \qquad [1]$$

and initial reaction parameters investigated were, set temperature range 350 to 500°C, deposition pressure 1.5 torr, precursor flow rate 1 to 10 sccm and hydrogen dilutent flow rate 700 sccm to 2 slm. Hydrogen plays a significant role in the decomposition of metal carbonyls and assists in the removal of reaction by-products. The deposition rates versus process temperatures of 350 to 500°C at 1 slm hydrogen, 1 sccm precursor (as measured by hydrogen MFC) and 1.5 torr pressure are given in figure 1. As the deposition temperature increases it can be seen that the deposition rate decreases. Depositions of pure (confirmed by XRD) low resistivity cobalt layers were achieved at set temperatures above 400°C with deposition rates varying linearly with precursor flow from 30 to 200 Å/min. At higher substrate temperatures the CVD chamber fittings will become hotter, leading to increased reaction between the cobalt precursor and the fixture. This could result in the starvation of Co precursor at the substrate surface. At 350°C the thickness of film could be due, in part, to a higher percentage of impurities in the layer. Reduced deposition rate with increasing temperature was also found by Lane (3) for APCVD and Ivanova (2) in LPCVD. AFM results for 450°C layers indicated an RMS roughness of approximately 15 nm for 3000 Å of cobalt.

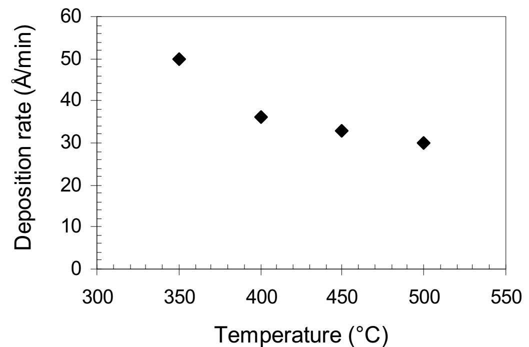


Figure 1. Deposition rate vs. Temperature

The magnetic properties of the films were measured by a vibrating sample magnetometer (VSM). The wafers were measured in 10 kOe magnetic fields at room temperature and the saturation of magnetisation (Ms) values are shown in figure 2 for layers deposited with 1 slm hydrogen, 1-10 sccm precursor flow and 1.5 torr pressure at 450°C. This shows that the thicker the film is, the higher the saturation of magnetisation. The magnetisation of our samples is less than that of bulk Co, which may be due to the impurities or to smaller cobalt grain sizes. Gangopadhyay (4) reported that the magnetisation increases with grain size. The decrease in magnetisation with decreasing grain size is due to the increased volume fraction of oxide in smaller grains. A best saturation of magnetisation of 800 emu/cc was obtained at 450°C with a lowest resistivity of 18 $\mu\Omega$-cm.

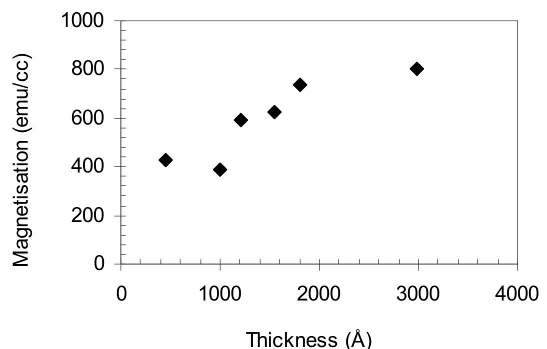


Figure 2. Magnetisation vs. Thickness

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