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In situ resistivity measurements during growth of ultra-thin $Cr_{0.7}Mo_{0.3}$

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Abstract

The growth of ultra-thin, lattice matched, $Cr_{0.7}Mo_{0.3}$ films on an MgO substrate, in a dc magnetron discharge, was investigated by in situ measurements in order to determine the minimum thickness of a continuous layer. The thickness dependence of the resistivity shows a coalescence thickness of less than two monolayers indicating layer by layer growth of the films. We compare the resistivity of the films to a combination of the Fuchs–Sondheimer and the Mayadas–Shatzkes models, assuming a thickness dependence of grain size. The model indicates that grain size increases with increasing growth temperature.

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1. Introduction

Recently there has been a growing technological interest in ultra-thin metallic conducting layers. They are used in nanoscale electronics as interconnects and diffusion barriers [1], in magnetic spin valves for magnetic data systems [2], and as electrodes in biosensors at the molecular level, where the subject requires dimensions in the nanometer range [3]. In some of these applications the resistance of the signal pathway will play a critical role in determining the operating frequency and/or sensitivity of the devices, as well as dictating the voltage drop and Joule heating of interconnects. As the thickness of the conductor approaches the size scale of the mean free path of the conduction electrons, size effects start limiting the conductivity of the film. Fuchs and Sondheimer [4] showed that loss of conductivity can be attributed to the scattering of the conduction electrons at the surface of the film. The scattering is characterized by a specularity parameter p, which represents the fraction of conduction electrons specularly scattered at the interface. If the thickness of the film is further reduced, the effects of interface roughness and grain boundaries lower the conductivity even more rapidly. Grain boundary effects have been studied by Mayadas and Shatzkes [5], and Namba [6] derived a model incorporating surface roughness. Conductor thickness is ultimately limited by the coalescence thickness, i.e. the thinnest film that will form a complete layer.

If a thin film of material A is deposited on a crystalline substrate of material B, different from material A, the way in which the atoms condense on the surface is influenced by the surface free energies of the two materials, crystal structure and lattice constant, and the chemical interaction between A and B [7]. Lattice mismatch between film and substrate causes strain in the film. Strain increases the free energy of the interface which can induce island formation [8] and thus a greater minimal thickness for film continuity, and increased roughness. Films can also develop dislocations to relax strain. These dislocations further degrade the conductance of metal films. By choosing a film material with compatible crystal structure and lattice constant, to that of the substrate, the odds of achieving the desired layer by layer growth are increased. Chambers et al. [9] suggested using an MgO substrate and a Cr_xMo_{1-x} alloy as

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film material, thereby achieving a better than 99% lattice match, for x in the range 0.56 to 0.80.

Ex situ measurements, of resistance as a function of film thickness, involve growing a series of samples of varying film thickness. In contrast, by continuously monitoring the resistance of a growing film, in situ, a complete thickness dependence curve can be obtained during growth of a single sample. The in situ method thus makes it practical to vary growth parameters, such as substrate temperature and bias, process gas pressure and film growth rate, and optimize processes based on the resulting resistivity curves. A study [10] of Cu films, grown in an rf-enhanced dc-magnetron sputtering discharge, found a coalescence thickness of 5 nm and showed that the resistivity ρ of the film had dropped down to ten times the resistivity of the bulk material ρ_0 at 8 nm. In measurements made ex situ, evaporated Cu films showed a coalescence thickness of 10 nm and a drop to 10 ρ_0 at about 12 nm [11]. Cr films, evaporated onto Corning glass substrates, have been found to conduct at 0.2 nm and reach 10 ρ_0 at 3 nm [12] and Ag films sputtered onto ZnO coalesced at 5 nm [13]. In a previous report [14], we discussed ex situ resistance measurements on $Cr_{0.63}Mo_{0.37}$ grown in a dc-sputtering discharge. A coalescence thickness of less than 0.4 nm was reported. The purpose of the present report is to explore the effects of substrate temperature on the coalescence thickness and resistivity of thin films of $Cr_{0.7}Mo_{0.3}$ alloy, grown on lattice matched MgO substrates.

2. Experimental procedure

Films of $Cr_{0.7}Mo_{0.3}$ alloy were grown in a direct current magnetron sputtering discharge in a vacuum system, pumped to a base pressure of 1×10^{-7} mbar. The films were co-sputtered from a 50 mm Cr and a 75 mm Mo sputtering targets of purity 99.98% and 99.95%, respectively. The process gas was argon at a pressure of 4×10^{-3} mbar and purity 99.999%. The alloy composition was controlled by regulating the current to the targets; the settings were 194 mA for Cr and 60 mA for Mo. The composition was calculated by applying Vegard's law [15] to the lattice constant of the resulting CrMo peak at $\simeq 62.5°$ in the $\theta-2\theta$ X-ray diffraction (XRD) scan of the films. For the thin films grown in this study, the peak was usually too weak to give an estimate of the film grain size from the peak width using the Scherrer formula [15], but the relative crystallinity of the films could be inferred by the height of the peak. The measurements were carried out with a Philips PW1710 diffractometer with an angular resolution of 0.005°, using a copper tube (CuK_α, wavelength 0.15406 nm). The substrate was MgO (100) of size $(5\times10\times1)$ mm, with one side polished to a surface roughness of less than 0.5 nm RMS, manufactured by Crystal GmbH, Germany. The samples were cleaned in triclorethylene, acetone and methanol ultrasonic baths prior to insertion into the vacuum chamber. Contact pads of thickness greater than 200 nm were grown from $Cr_{0.7}Mo_{0.3}$ in such a way that a square of (5×5) mm uncoated MgO was left in the middle of the sample. Once under vacuum, the substrates were outgassed and annealed for 10 min at 700 °C. Films were grown at substrate temperatures of 24, 200, and 400 °C. The substrate was electrically isolated from the chamber. After deposition, each of the three samples was removed from the vacuum and the growth rate determined by cleaving off the contact pads, measuring the film thickness with a low angle X-ray reflection measurement, ex situ, and dividing by the deposition time (600 s). The error in the thickness determination is no more than 10%. Surface roughness was also estimated from the low angle X-ray reflection measurements.

The resistance of the growing film was measured with a simplified version of the dual lock-in amplifier setup described by Barnat et al. [16], suitable for measurements without a substrate bias. The setup is a standard four point probe resistance measurement, based on measuring both the voltage over the film, directly, and the current passing through the film, indirectly, by monitoring the voltage over a 50 Ω resistor in series with the film, thus eliminating the effect of contact resistance. The resistance of the thick contact pads, grown prior to the measurement, was found to be less than one ohm, an order of magnitude less than the lowest resistance measured over the film. Hence the resistance of the contact pads can safely be ignored and the pads assumed equipotential surfaces. A function generator (Tabor 8021) was used to generate a 600 mV RMS sinusoidal signal at 417 Hz. The resistivity of the films was calculated by multiplying the measured resistance with thickness and then correcting for asymmetries in the length and width of each sample, as measured by vernier calipers. Data was collected four times per second with a PC. The deposition time was measured with a stopwatch and the start of growth determined by subtracting the deposition time from the endpoint of growth, obviously visible from the measured curve. The total error in this determination is at most 4 samples, corresponding to ±0.03 nm in thickness, at the determined growth rate of 0.03 nm/s. The substrate holder is made from Macor ceramics to electrically isolate the four probe tips from each other. During growth, the probes and connectors are shielded from the flux of sputtered particles with a thin

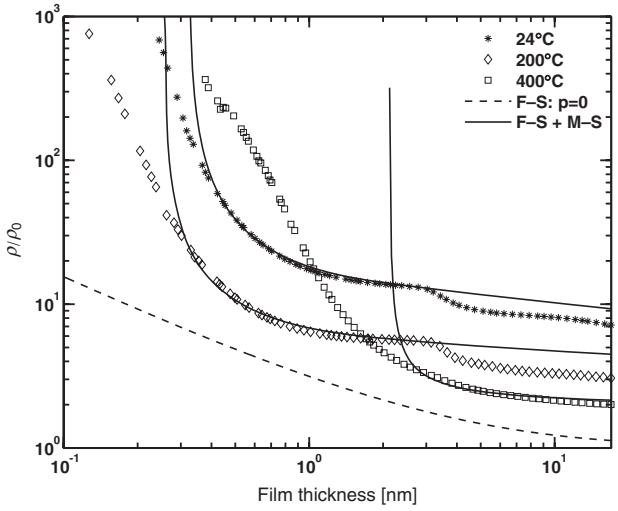

Fig. 1. The electrical resistivity, normalized by the bulk resistivity, as function of thickness of $Cr_{0.7}Mo_{0.3}$ films grown at three different substrate temperatures.