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The effect of argon pressure, residual oxygen and exposure to air on the electrical and microstructural properties of sputtered chromium thin films

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ABSTRACT

Chromium thin films were deposited on SiO_2/Si wafers using two sputtering systems with different levels of cleanliness, and at argon sputtering pressures varying between 0.13 and 0.93 Pa. Films from the two systems grown under identical sputtering conditions had significantly different resistivity values that are shown to be due to differences in residual oxygen in the chambers. Electrical transport measurements were conducted on the series of grown films to investigate the influence of argon pressure on film electrical resistivity. The films morphology, microstructure and composition were characterized using scanning electron microscopy and X-ray photoelectron spectroscopy. Significant differences were found in Cr thin films sputtered at different sputtering pressures; differences in resistivity performance and microstructure were noted. This change was shown to be due to the transition from porous structure to a denser microstructure. The Cr films sputtered at high pressure contained large quantities of oxygen when exposed to air. Some of the oxygen is added to the film during the deposition depending on the deposition rate and the base pressure of the sputtering system. The rest is incorporated into the film once it is exposed to air. The amount of oxygen added at this stage depends on the structure of the film and would be minimal for the films deposited at low sputtering pressures.

1. Introduction

Chromium (Cr) thin films are used in the fabrication of masks for integrated circuit photolithography, diaphragms and mirrors for microelectromechanical systems, as an adhesion layer for gold films, and as thin film resistor material [1]. Cr has also been widely studied as an archetypal band antiferromagnet [2,3]. Furthermore, Cr is a spin density wave (SDW) material and recent research has focused on SDW properties of Cr thin films [4] as well as resonant impurity scattering in these materials [5]. Cr thin films also have been shown to have very high resistivity [5–8] that depends on sputtering pressure.

The relationship between the microstructure of thick films (25 to 250 μm thick) and the sputtering pressure and temperature was developed by Thornton [8–10]. This structural zone model has been further refined to include thin films down to 100 nm, nanostructure as well as microstructure, and the reduction of the temperature and pressure variables to one energy variable [11]. The role of oxygen in the deposition system has been shown to retard structure growth for evaporated Al thin films [12]. In Thornton's Zone Model there are several zones of microstructure that develop in films depending on the sputtering pressure and the homologous temperature, T_H. At low T_H and higher sputtering pressures the film microstructure consists of tapered crystallites with voided intergranular boundaries (zone I). This leads to a porous structure which has poor lateral strength and low density [9]. At higher T_H the structure consists of a transition structure that is made up of densely packed but poorly defined fibrous grains that are separated by nearly conventional grain boundaries (zone T) [9]. Metal coatings with the transition structure exhibit high optical reflectance, moderate and relatively low resistivity, and a state of compression [13–15]. At even higher T_H and all pressures the structure consists of columnar grains separated by dense intercrystalline boundaries (zone II), and at the highest T_H and all sputtering pressures the structure consists of recrystallized equiaxed grains (zone 3) [16].

In this research, Cr thin films were deposited on oxidized Si wafers using two sputtering systems with different levels of cleanliness, and at argon sputtering pressures varying between 0.13 and 0.93 Pa. Electrical transport measurements were conducted on these films to investigate the influence of argon pressure on film electrical resistivity. The films morphology, microstructure and composition were characterized using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The resistivity performance and the microstructure of sputtered Cr thin films under different sputtering pressure were found to have significant differences. This change was shown to be due to the transition from a porous structure to a denser microstructure. Furthermore, it is shown that the resistivity change can be used to locate the boundary between these microstructures. The Cr films sputtered at high pressure contained large quantities of oxygen after exposure to air. This oxygen was shown to be due to the formation of a native oxide on the surface of

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the porous Cr grains. Optical measurements were also performed to investigate the effects of deposition pressure on the optical properties.

2. Experimental procedure

Thin films of Cr were prepared by DC magnetron sputtering. Two sputtering systems were used in the experiments: sputtering systems #1 and #2. Most of the films were grown in sputtering system #1, a load locked system with a base pressure below 4.0×10^{-5} Pa. For runs done in both systems the gun power was 300 W DC, there was no substrate heat, and the Ar gas pressure was varied between 0.13 Pa and 0.93 Pa. Both systems used 75 mm diameter × 6.4 mm thick Cr metal targets with 99.95% purity, a common Ar high purity (99.998%) gas supply, and both units had cryopump high vacuum systems. Under these conditions, the deposition rate of Cr was 0.27 nm/s for 0.13 Pa argon pressure and 0.38 nm/s for 0.93 Pa argon pressure. To investigate the effect of base pressure on film resistivity, a series of Cr thin films were deposited in sputtering system #2. This system had a base pressure $<3.2\times10^{-4}$ Pa, and since the chamber was exposed to air each time a sample was loaded, it was expected that the level of absorbed gases, such as water vapor, would be much higher than in system #1.

Oxidized Si (100) wafers and microscope slides were used as substrates in these experiments. The Si wafers were cleaned in a standard piranha solution (sulfuric acid and hydrogen peroxide mix) followed by a thermal oxidization process that formed a 200 nm SiO_2 layer on the wafers. Microscope slides were cleaned in isopropanol and dried in nitrogen. 150 nm Cr films were deposited for resistivity measurement. Film resistivity was obtained from sheet resistance data measured by a four point probe and the film thickness measured by stylus profilometry. The surface morphologies of the Cr films were imaged using a SEM (JEOL JAMP-9500 F Field Emission Auger Microscope). To determine the surface composition of the films, XPS analysis was performed on a Kratos Analytical AXIS-165 spectrometer at the Alberta Centre for Surface Engineering and Science (ACSES). The base pressure in the analytical chamber was lower than 3×10^{-8} Pa. A monochromatic Al K_α ($h\nu=1486.6$ eV) source was used at a power of 210 W. Survey spectra were collected for binding energies ranging from 1100 to 0 eV with pass energy (PE) of 160 eV and step of 0.35 eV. High-resolution spectra were measured with PE of 20 eV and step of 0.1 eV. A 4 keV argon ion beam was used for depth profiling. The beam was scanned with an amplitude of ±1.5 mm in the x and y directions.

Optical properties of the films deposited on Si (100) substrates were measured using a Variable Angle Spectroscopic Ellipsometer (VASE) from J. A. Woollam Inc. The spectroscopic data was acquired at an angle of incidence of 75° over the spectral range of 1.5 to 4.1 eV. WVASE32 software was used for generation of model data and fitting to the experimental data. Spectroscopic measurements were performed on 10-nm-thick Cr films deposited on silicon substrates.

3. Results and discussion

A two dimensional representation of the zone model is shown in Fig. 1 with different regions of microstructure that depend on sputtering temperature and pressure. This diagram is based on Thornton's “Zone Model” [8,9] which was founded on the microstructural observation of thick metal films. The diagram is divided into four zones. Due to equipment operating limitations, the sputtering experiments were performed at room temperature. Since the homologous temperature of Cr is 0.14 at 300 K, with the variation in argon pressure from 0.13 to 0.93 Pa, the thin films would have microstructures changing from zone T to zone I as the sputtering pressure is increased. Zone I has a porous structure, consisting of tapered crystallites separated by voids. If exposed to air, the thin film will quickly oxidize leading to degraded purity and high resistivity. Zone T, however, has a transition structure of densely packed fibrous

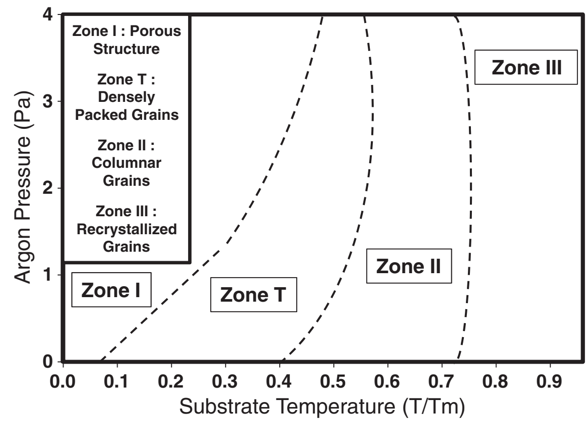

Fig. 1. Schematic diagram showing the influence of argon pressure and substrate temperature on microstructure of sputtered metallic films, reproduced from [8].

grains. The thin films in zone T would be in compression and have low resistivity.

3.1. Electrical resistivity

The electrical resistivity of metal thin films is a sensitive indicator of the structure and purity of the films [17]. In order to understand the impact of the base pressure on the resistivity of Cr, thin films were grown in two different sputtering systems with different base pressures, as shown in Table 1. Films grown in sputtering system #2 have resistivity values more than two times greater than the values obtained in system #1 at 0.23 Pa argon pressure and 35% higher at 0.8 Pa. However, the increase in resistivity at both pressures is ~40–60 μΩ cm. The only difference between the two sputtering systems is the quality of the base pressure. Base pressure governs the amount of residual oxygen in the sputtering system. The amount of oxygen incorporated into the growing Cr films and can be estimated from the growth rate of the Cr films, and the impingement rate, N_i, of the residual oxygen in the chamber, where $N_i = P(2\pi mk_BT)^{-\frac{1}{2}}$ and N_i has units of molecules $cm^{-2}\ s^{-1}$, P is the partial pressure of oxygen in the vacuum chamber, m is the mass of the oxygen molecule, k_B is Boltzmann's constant, and T is temperature in Kelvin [18]. From the equation for N_i, the residual oxygen flux impinging on the growing film is directly proportional to P. Assuming T = 300 K and that the partial pressure of oxygen in the chamber is ~0.21 of the total pressure (same ratio as oxygen in air at standard temperature and pressure), we get $P1_{O2}=8.20\times10^{-6}$ Pa for system #1 and $P2_{O2}=6.72\times10^{-5}$ Pa for system #2. A Cr deposition rate of 0.38 $nm\cdot s^{-1}$ (0.93 Pa argon pressure) gives a Cr flux of 5.24×10^{14} atoms $cm^{-2}\ s^{-1}$, and the O flux for system #1 is 4.41×10^{13} atoms $cm^{-2}\ s^{-1}$ and for system #2 it is 3.61×10^{14} atoms $cm^{-2}\ s^{-1}$. This gives an approximate atomic oxygen concentration of 8% for system #1 and 40% for system #2. These values are only estimates since this is a simplified calculation. The oxygen sticking coefficient is assumed to be one and the influence of molecular pumping speed on the partial pressure of gases at base pressure is ignored. The value for system #2 appears to be high since

Table 1
The effect of sputter system base pressure on the Cr film resistivity at 0.23 and 0.80 Pa Ar sputtering pressure.

Sputter	Resistivity, μΩ cm	
System	$P_{Ar}=0.23$ Pa	$P_{Ar}=0.80$ Pa
#1	33.3	168.4
#2	78.1	236.0