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Fabrication of ferromagnetic and antiferromagnetic chromium oxides by organometallic chemical vapor deposition

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We have been able to fabricate CrO and Cr2O3 from ultraviolet photolytic and plasma-assisted decomposition of Cr(CO)6 in an oxygen carrier gas. The composition of these films is uniform in composition and contains little contamination. Using magneto-optic Kerr effect measurements, we have been able to demonstrate that the CrO films are ferromagnetic.

INTRODUCTION

The decomposition of the hexacarbonyls, M(CO)6 (where M is Cr, Mo, or W), to form metal thin films has been the subject of a great number of studies.1 While a number of investigations have been directed toward fabricating chromium films from the decomposition of chromium hexacarbonyl, the quality of the resulting films has varied from films with only limited amounts of oxygen contamination (less than 7% oxygen and 0.8% carbon)2,3 to the more typical films with large amounts of oxygen and carbon contamination.4,5 The propensity for films formed from the decomposition of chromium hexacarbonyl to incorporate contaminants, particularly oxygen,5,6 during film growth can be exploited to form technologically important thin-film materials. In particular, we have chosen to promote the incorporation of oxygen by decomposing chromium hexacarbonyl in an oxygen atmosphere.

The selected area deposition of CrO thin films, possible with organometallic chemical vapor deposition, is important because CrO, is a ferromagnetic compound at room temperature with a Curie temperature 118 °C (Ref. 10) with a number of technological applications. Furthermore, this compound can be demagnetized with little input of energy and has pronounced magneto-optic properties in the visible including a substantial Kerr effect.7

EXPERIMENT

The chromium oxide films were deposited by photolytic and plasma deposition of Cr(CO)6 in ambient oxygen atmosphere. The Cr(CO)6 was introduced into each vacuum system from the sublimation of the crystalline solid, whose vapor pressure is given by9,12

$$\log_{10} P = 10.63 - 3285/T$$

where $P$ is the pressure in Torr, and $T$ is the temperature of the hexacarbonyl in degrees Kelvin.

The vacuum system for pyrolytic and photolytic CVD has been described elsewhere.1,14 The photolytic decomposition of Cr(CO)6 was performed with a commercial (Moletron) pulsed nitrogen laser in the near ultraviolet (337 nm). The power output of the laser was 130 mW with a peak output of 450 kW or 4.5 mJ/pulse. The beam dimension was 6 mm × 32 mm and focused through a quartz window on a silicon wafer to a 0.4 mm × 2.1 mm area. The substrate holder was a solid copper block which could be cooled with chilled water. Photolytic deposition times ranged in periods from 3 to 48 h. The background pressure in this all-glass vacuum system was approximately 10−3 Torr. The organometallic complexes were admitted to a pressure no more than 10 m Torr.

Chromium oxides were also deposited using a 13.56-MHz, 200-W rf plasma. This system could reach a base pressure of 10−3 Torr. The silicon substrates could be heated by a cartridge heater to a temperature of 150 and 300 °C. A continuous flow system was used with all deposition techniques, with an oxygen carrier gas supplying additional background pressure. The plasma assisted deposition chamber is schematically shown in Fig. 1.

The coatings were examined while still in place on the silicon by scanning microscopy (SEM), x-ray emission spectroscopy (XES or EDAX), Auger electron spectroscopy (AES), and magneto-optic Kerr effect (MOKE). In order to determine the composition of the films produced either by rf plasma-assisted deposition or by laser-assisted deposition, Auger depth profiling was undertaken using a commercial Perkin-Elmer Auger electron spectroscopy system. The determination of the film thickness was undertaken using a commercial mechanical film thickness probe (Talysurf 4).

The magneto-optic Kerr effect measurements were performed using a 5-mW He-Ne laser, two crossed polarizers, and a chopper wheel run at 800 Hz. All measurements were performed in air. The maximum applied magnetic field was 1500 Oe, and the applied field was changed at the rate of 15 Oe/s. The signal was obtained using a lock-in amplifier. The light was detected using a photodiode and transduced to a voltage.

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PHOTOLYSIS

The great potential of photolytic deposition of Cr(CO)₅ is that photolysis of surface species may be used for selective area processing. We have been able to selectively deposit Cr₂O₃, using 1 mTorr oxygen and 10 mTorr of Cr(CO)₅, with the laser decomposition from a nitrogen laser. The formation of Cr₂O₃ requires far higher partial oxygen pressures.

From our Auger electron spectroscopy results, it is clear that both Cr₂O₃ and Cr₂O₅ can be formed (Fig. 2). The composition of the films with depth into the film has been investigated by ion milling of the film with Ar⁺ -ion bombardment and compositional analysis with Auger electron spectroscopy. These Auger depth profiling studies show that the films fabricated by the laser assisted decomposition of Cr(CO)₅ in any oxygen atmosphere are uniform except for an interfacial region in the vicinity of the silicon substrate surface (Fig. 2). Earlier studies have shown that Cr₂O₃ is readily formed via laser-assisted decomposition of the chromium hexacarbonyl. There have also been early indications that chromium dioxide could be formed as well. The results, outlined in Fig. 2, demonstrate that both oxides can be readily formed reproducibly into reasonably isotropic films.

We have observed that the rate of chromium deposition can differ by a factor of 3 over 6° (288–294 K), under identical conditions, for different substrate temperatures using XES as a measure of film thickness. This is a strong indication that the decomposition process is a surface process. At lower temperatures, the surface lifetime of the organometallic species is much longer than the probability of being able to remove a carbonyl ligand rather than initiate desorption into vacuo may be reasonably expected to be greater. Given the bond strength of the carbonyl ligands to the metal and the results of surface studies with a variety of carbonyls (see, for example, Ref. 15 and 16), it is clear that the laser decomposition of the chromium hexacarbonyl occurs through the sequential removal of carbonyl ligands, even with radiation in the ultraviolet (in our case, 337 nm).

For very rapid thin-film growth, where selective area processing is not required, plasma-assisted deposition of chromium oxides can be undertaken, as discussed below.

PLASMA-ASSISTED DEPOSITION

By operating the plasma reactor at 10-W power, with the sample temperature of 242 °C and a Cr(CO)₅ pressure of 10μ, a chromium oxide film can be deposited. With a partial pressure of oxygen between 3 and 15μ, we have found that the film composition is uniformly Cr₂O₃ as determined by Auger depth profiling. Fabrication of Cr₂O₃ requires oxygen partial pressures greater than 15μ.

In spite of the very large number of competing reactions expected in plasma-assisted decomposition of Cr(CO)₅, sequential carbonyl ligand removal does appear to occur and the films are surprisingly free of contamination as seen in Fig. 3. Mass spectroscopy studies of the metal hexacarbonyls clearly indicate that the sequential removal of carbonyl ligands is the preferred decomposition route under electron impact. We believe that, as with most plasma-assisted decomposition processes, electron impact is one of the most important decomposition mechanisms. Very little carbonyl incorporation is observed to occur in spite of the very rapid rate of film growth. The rate of thin-film growth under our operating conditions is approximately 30 Å/min.

MOKE studies were undertaken of these films, and the Cr₂O₃ films provided some evidence for ferromagnetism. While the signal level was satisfactory for MOKE, the signal-to-noise ratio was poor as a result of scattered light from the thin-film surface. Nonetheless, the hysteresis loop for Cr₂O₃ obtained from MOKE does show that these films are...
ferromagnetic, as seen in Fig. 4. Both the MOKE hysteresis loop and the Auger electron spectroscopy studies of composition provide clear indications that we can form antiferromagnetic chromium oxides. This can be accomplished by raising the temperature of the substrate and/or lowering the oxygen partial pressure within the plasma. These films are also uniform in composition.

We have observed that the CrO$_2$ films are not uniformly ferromagnetic and have a wide range of coercivities. Indeed, some areas of these films appear to be antiferromagnetic. At present, these results are not completely understood, and we need to identify the precise conditions for making CrO$_2$ films that have uniform ferromagnetic properties as well as uniform composition. Auger electron spectroscopy studies provide some evidence for oxygen and chromium interdiffusion. Given that the Cr$_2$O$_3$ oxide is more stable at the temperatures of our thin-film growth, it is not surprising that we observe CrO$_2$ precipitates at the chromium oxide-silicon interface. These chromium oxide islands may contribute to the nonuniform ferromagnetic properties of our films, as observed in our MOKE studies.

Scanning tunneling microscope studies of these films are in progress to study their morphology on an atomic scale.  

**CONCLUSION**

We have demonstrated using MOKE that ferromagnetic CrO$_2$ films can be fabricated from the decomposition of Cr(CO)$_6$ in an oxygen atmosphere. The advantages of this type of thin-film fabrication are the very low processing temperatures and the potential for selective area processing. The films can be fabricated with surprisingly little contamination and considerable compositional uniformity. Silicon does not, however, appear to be an ideal substrate as a result of interdiffusion or chemical reactions that occur at the silicon chromium oxide interface.

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