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MAGNETIC FIELD EFFECT TRANSISTORS

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It has been demonstrated that magnetic CrO_2 can be selectively deposited on semiconductor substrates and polymide resin plastics with feature resolution smaller than 1μm. In addition, hard coatings have been fabricated to protect active devices as well as developed new techniques for fabricating conventional devices such as p-n junctions, from organometallic and main group complexes.

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The goal of this project was to demonstrate that real time selective area deposition of conducting magnetic thin films and hard coatings could be accomplished with the photolysis of organometallic complexes.

Magnetic Films

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 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 [4-9]. The propensity for films formed from the decomposition of chromium hexacarbonyl to incorporate contaminants, particularly oxygen [6,9] 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 decomposition of CrO_2 thin films, possible with organometallic chemical vapor deposition, is important because CrO_2 is a ferromagnetic compound at room temperature with a Curie temperature 118°C [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 [11].

A-1

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 by [8,12]

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

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 [13,14]. The photolytic decomposition of $Cr(CO)_6$ was performed with a commercial (Molectron) pulsed nitrogen laser in the near ultraviolet (337 nm). The power output of the laser was 330 mW with a peak output of 450 kW or 4.5 mJ/pulse. The beam dimension was 6 mm x 32 mm and focused through a quartz window on a silicon wafer to a 0.4 mm x 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 hours. The background pressure in this all glass vacuum system was approximately 10^{-5} Torr. The organometallic complexes were admitted to a pressure no more than 10 milliTorr.

The coating 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). The SEM studies were performed using ISI Super II, with an attached Kevex 5500 X-ray spectrometer. The energy of the primary electron beam was 25 keV. The XES spectra were recorded using an SiLi X-ray detector and a multichannel analyzer to produce a spectrum as a function of X-ray photon energy. XES spectra provided some

elemental composition analysis from the characteristic X-ray lines. The X-ray spectrometer was insensitive to oxygen and was also unable to detect either carbon or hydrogen.

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 films thickness probe (Talysurf 4).

The magneto-optic Kerr effect (MOKE) 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/sec. The signal was obtained using a lock-in amplifier. The light was detected using a photodiode and transduced to a voltage.

The great potential of photolytic deposition of $Cr(CO)_6$ is that photolysis of surface species may be used for selective area processing [1-7,9]. We have been able to selectively deposit Cr_2O_3 using 1 mTorr oxygen and 10 mTorr of $Cr(CO)_6$ with the laser decomposition from a nitrogen laser. The formation of CrO_2 requires far higher partial oxygen pressures.

From our Auger electron spectroscopy results it is clear that both Cr_2O_3 and CrO_2 can be formed (Figure 1). 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 $Cr(CO)_6$ in an oxygen atmosphere are uniform except

for an interfacial region in the vicinity of the silicon substrate surface (Figure 1). Earlier studies have shown that Cr_2O_3 is readily formed [9] via laser assisted decomposition of the chromium hexacarbonyl. There have also been early indications that chromium dioxide could be formed as well [6]. The results outlined in Figure 2, demonstrate that both oxides can be readily formed reproducibly into reasonably isotropic films.

From XES spectra of the films we can see that there is clear evidence of chromium deposition, and from the chromium to silicon ratios, we can estimate the film thickness. It is clear that the rate of chromium deposition can differ by a factor of three over six degrees, under identical conditions, for different substrate temperatures. The temperature dependence of the chromium oxide deposition between substrate temperatures of 288 K and 294 K 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, and 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 [1] and the results of surface studies with a variety of carbonyls (see for example references [15,16]) 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).

The cross-section of gaseous $Cr(CO)_6$ is much greater at shorter wavelengths closer to 230 nm, though the deposition rate of chromium is observed to be substantial at longer wave lengths far from the gaseous $Cr(CO)_6$ absorbance maximum [15]. Adsorption is noted to shift the optical absorption

bands of organometallic species [1], and a substantial decomposition rate from absorption of light at 337 nm is not surprising.

Formation of CrO_2 from the photolysis of chromium hexacarbonyl results in relatively smooth films for deposition at substrate temperatures of 294 K while films formed at higher substrate temperatures of 315 K are uneven. From depth profiling studies, it is abundantly clear that at higher temperatures both oxygen and chromium interdiffuse into the silicon substrate. This leads to non-uniform compositions at the interface of the chromium oxide and silicon. The film morphology is also complicated by surface nucleation (catalytically reactive regions where rapid growth occurs [1]) as well as interdiffusion, though for very rapid overlayer film growth is observed to lead to far more uniform films, particularly for plasma assisted deposition.

For very rapid thin film growth, where selective area processing is not required, plasma assisted deposition of chromium oxides can be undertaken. These films of CrO_2 are patently magnetic as evidenced by MOKE.

Wire Interconnects

Fabrication of VLSI components on dielectric materials and flexible plastics is, of course, of enormous technical importance. To show that this technology is possible, we have selectively deposited conducting wires and resistors on polyimide substrates.

We have demonstrated that the selective area deposition of palladium on polyimide substrates is possible through the U.V. photolysis of (π-allyl) (π-cyclopentadienyl) palladium. This photolytic deposition process did not result in any apparent damage to either the Ultem 1000 (polyetherimide) or

Kapton substrates. The resistivity of the palladium films (<0.1 um) suggests that the films are porous.

The films are free of contamination. The adhesion of the palladium films to the substrates is very good and has been demonstrated to be suitable for applications including interconnects and in thin film resistors.

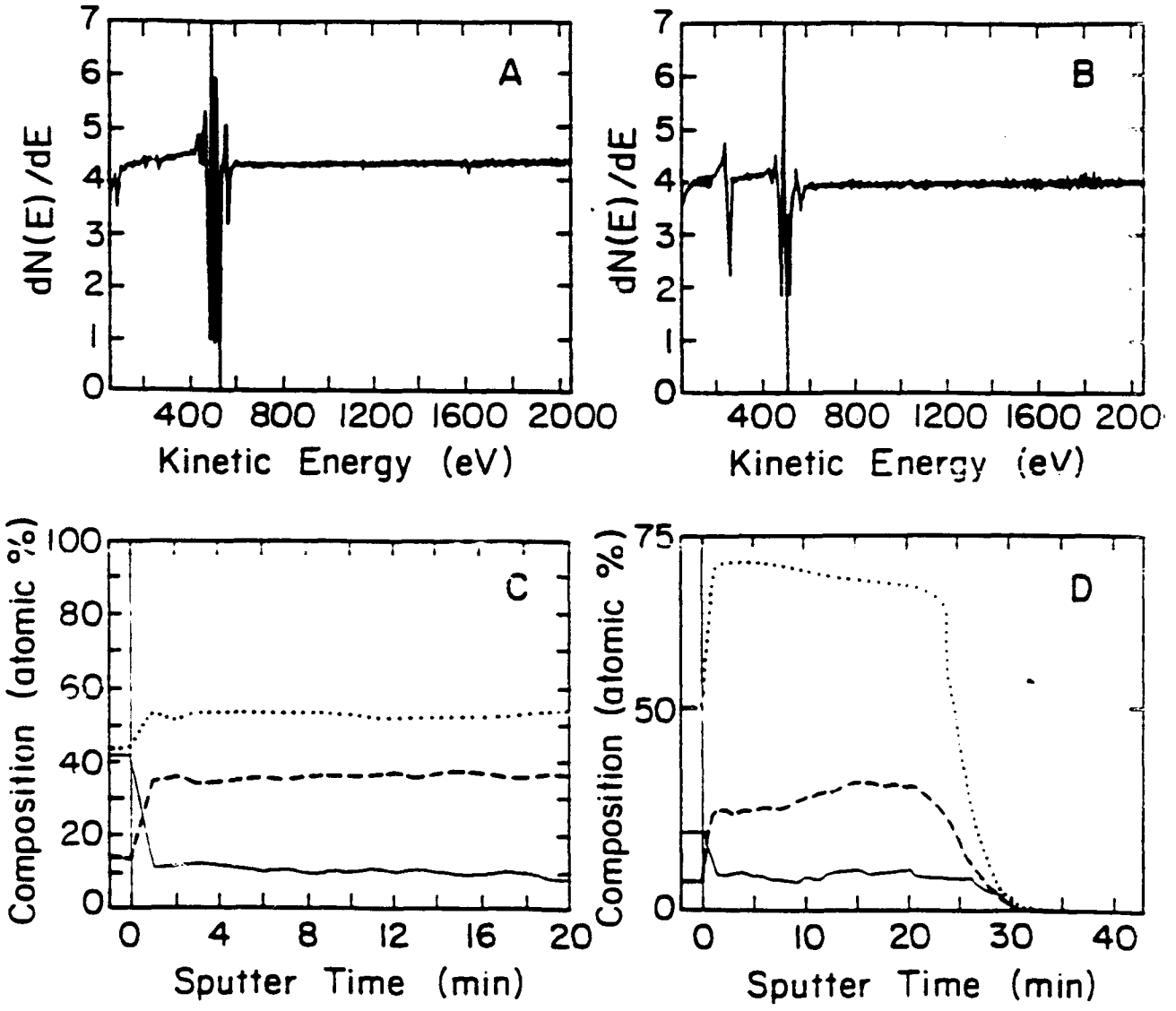

Figure I: Auger electron spectra of Cr_2O_3 (A) and CrO_2 (B) films fabricated from the photolysis of $Cr(CO)_6$ in oxygen at 337 nm. Auger electron spectroscopy depth profile provides a strong indication that these films have a uniform composition for the Cr_2O_3 (C) and CrO_2 (D).

The polyimide substrates were exposed to a vapor of $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)Pd)$ for between 17 and 19 hours while irradiating the substrate with the laser beam. Upon conclusion of the irradiation, palladium was found to be deposited. Confirmation of the presence of palladium was obtained from XES. The deposited film was compared to a pure palladium standard. The XES spectrum for palladium on Ultem 1000 is similar to that of bulk palladium. Film thickness was determined from XES and WDS, and the correlation of the data to model scattering calculations are good. Scratches through the films on Kapton and Ultem 1000 did not reveal the presence of any obvious damage to the polyimide films and, in general, the palladium films were found to adhere well to the substrates.

The conducting strips were deposited so that the film thickness was varied along the strip (approximately 500 Å thick at one end but with a decreasing thickness along the length of the strip). By depositing this wedge shaped strip across previously deposited copper lines spaced equally approximately 980 um apart we were able to determine the approximate volume resistance of the palladium film for a variety of thicknesses. This is shown in Figure 2.

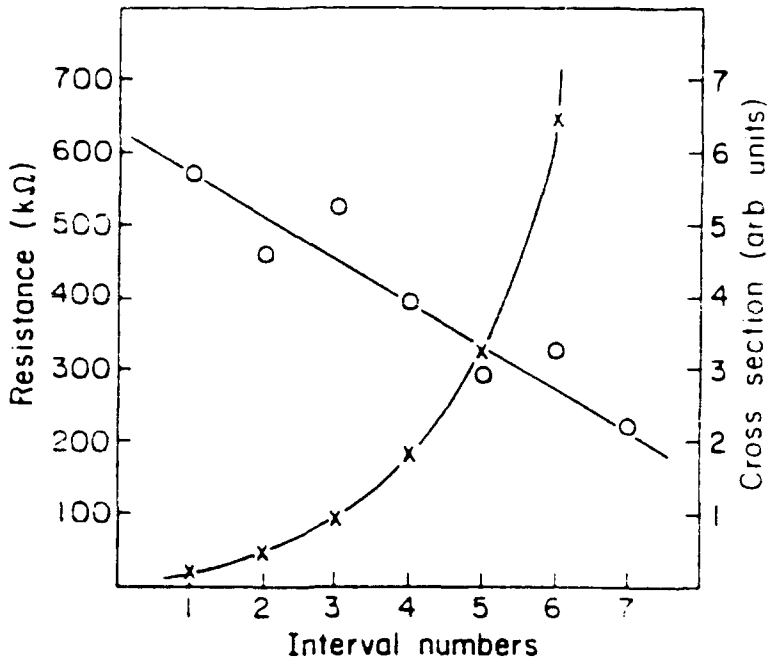

Figure 2 – Resistance (o) and cross-sectional area (x) as a function of interval numbers.

By replotting the data against the palladium strip cross sectional area, it is apparent that the volume resistivity and the conductance of the palladium film is dependent on the film thickness. This is shown in figure 3.

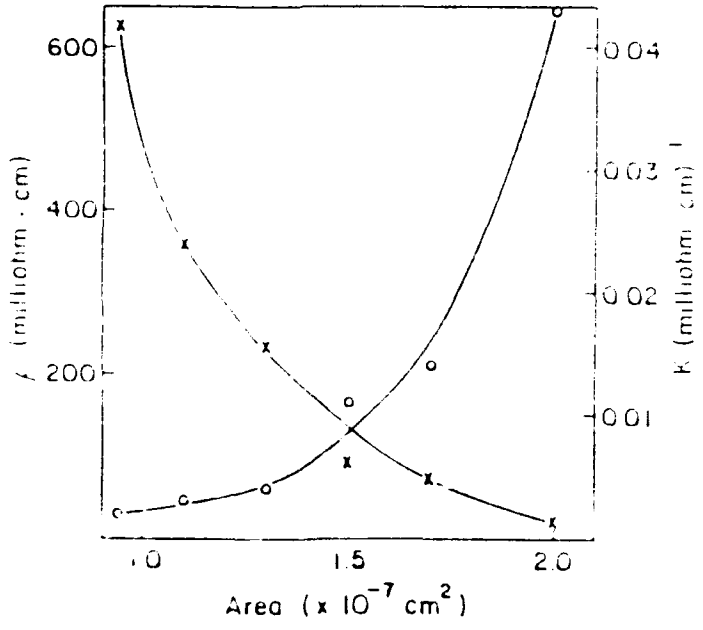

Figure 3 – Volume resistivity (x) and Conductivity (o) as a function of area.

Hard Protective Coatings

Our studies indicate that $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ are not optimal source compounds for the deposition of pure metal films by organometallic chemical vapor phase deposition. In contrast, molybdenum carbide coatings can be readily formed from $Mo(CO)_6$ decomposition and these films have many desirable properties required for hard protective coatings. While the formation of uniform films from the photolytic or pyrolytic decomposition of $Mo(CO)_6$ may prove to be difficult, we suggest that plasma deposition provides a means for fabricating reproducibly uniform films but that these films will be contaminated with oxygen and/or carbon impurities.

Conventional Semiconductor Devices

By combining synchrotron radiation with photolysis of boranes, we have been able to fabricate large arrays of convention diodes on Si(111). The U.V. photolysis of boranes permits one to deposit boron selectively on n-type silicon to permit doping to p-type. The resulting p-n junction is well characterized.

Conclusion

The above techniques, when combined, should make it possible to explore the fabrication of conventional and novel devices in "real time" on a variety of substrates possibly including flexible high temperature plastics. The selective area process capabilities and the potential for avoiding post deposition annealing treatments should make it possible to include materials and structures that are not the equilibrium structures. Such devices may have

potential special applications, such as unusual optical properties, as well as for providing an alternative to conventional devices and permitting repair "insitu" of VLSI arrays.

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