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Li Yan
University of Nebraska - Lincoln

John A. Woollam
University of Nebraska - Lincoln

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Optical modeling of iridium thin film erosion under oxygen plasma exposure*

Li Yan and John A. Woollam
Center for Microelectronic and Optical Materials Research, and Department of Electrical Engineering, University of Nebraska-Lincoln. Lincoln, Nebraska 68588-0511

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This work is motivated by interest in use of iridium metal films in the space environment. Optical metrology is a sensitive tool for study of film roughness, optical constants, and microstructural properties. In the present paper, *in situ* spectroscopic ellipsometry is applied to monitor oxygen plasma etching of films of iridium/chromium on fused silica substrates, using an electron cyclotron resonance plasma source. Optical modeling allows for a fundamental understanding of the plasma etching mechanism. Analysis of spectroscopic psi and delta data at selected time slices suggests the iridium film is etched away gradually upon plasma irradiation, while showing no signs of oxidation or other chemical changes. Nanoscale atomic mixing and index of refraction grading are observed. © *2004 American Vacuum Society.* [DOI: 10.1116/1.1781182]

I. INTRODUCTION

Iridium (Ir) is used as a reflecting surface in NASA's x-ray telescope.[1] For this use, extremely low-roughness surfaces are needed, as well as a surface with virtually no oxidation. In addition, iridium metals are currently being considered as substrates for the study of contamination layers deposited on spacecraft surfaces. High vacuum plus particle and photon fluxes in the low earth orbit (LEO) environment induce material sputtering, outgassing, and consequent deposition on, and contaminations of sensitive surfaces. Contaminations from evaporated or sputtered silicones are an important example. In an effort to identify these sources of contamination, an in-space experiment entitled, "Polymers Erosion and Contamination Experiment" (PEACE), has been designed and proposed.[2,3] To that end, NASA first needs to find an appropriate substrate onto which the ultimate contamination can land (or deposit) for further study. Among candidate materials, iridium seems promising because of its unique properties, including smooth surfaces, high melting point (~2713 K), low vapor pressure, low oxygen permeability, and high chemical stability, to name a few.[4–7] For use in space, the substrate itself has to have superb stability in the adverse environment in space.

This work is motivated by NASA's interest in the use of iridium in the space environment. In addition, fundamental optical constants of metals have been difficult to measure, due to the strong influence of roughness and/or hydrocarbon overlayers.[8] As reported by our group recently, extremely smooth thin films of iridium were deposited using dc magnetron sputtering, and their optical constants determined using variable angle spectroscopic ellipsometry (VASE®), over the spectral range from vacuum ultraviolet (UV) to middle infrared (IR) (140 nm–35 um).[9] The effects of roughness on apparent optical constants were carefully removed in the film analysis; therefore the final determined optical constants are expected to be the best available for Ir metals, minimally affected by surface overlayers or surface microstructure.

The aim of the present work is to study the rate and nature of erosion of as-deposited Ir films under exposure to an electron cyclotron resonance (ECR) generated oxygen plasma. *In situ* ellipsometry has been employed as a nonintrusive diagnostic tool to investigate (in real time) the interactions between the reactive plasma and the sample surface. The emphasis of the work reported in this article is towards optical modeling of bulk metals under plasma irradiation. To date, little work has been published in this area due to the potential difficulties involved, including lack of suitable diagnostic techniques, complexity of the processes, etc. The actual optical modeling obviously is process dependent; but the basic concepts developed here should lend themselves well to analysis of other metals and/or plasma sources.

II. EXPERIMENT

A. Film preparation

The iridium film studied here was deposited onto a superpolished fused silica substrate of 1 in. diameter and 1/4 in. thickness. The backside of the substrate was roughened for the sake of eliminating back-side reflected light in ellipsometry measurements. The film was dc magnetron sputter deposited at 35 W from an Ir target in an argon atmosphere at 5 mTorr pressure. The substrate to target spacing was 10 cm. Deposition lasted 20 min, yielding an optically thick Ir layer. To help the Ir film to better adhere to the fused silica surface, a chromium (Cr) layer of ~14 nm thickness was first deposited as a buffer. Vacuum was not broken between Cr and Ir depositions. Details on preparation of the Ir films are described elsewhere.[9]

B. Ellipsometry

Ellipsometry is an optical technique using polarized light to probe the dielectric response of a sample.[10] Reflection ellipsometry measures the change in the polarization state of

*No proof corrections received from author prior to publication.

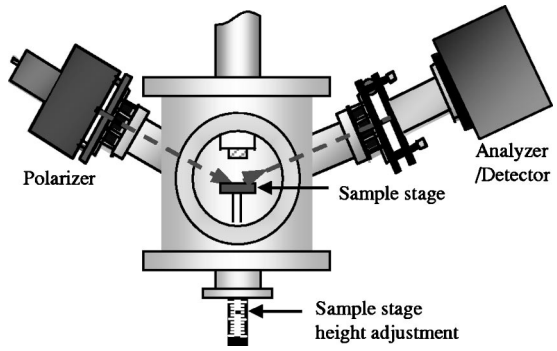


FIG. 1. ECR oxygen plasma chamber.

light as it reflects from a sample surface. The measurement is expressed in terms of psi (Ψ) and delta (Δ):[11]

$$\rho \equiv \tan(\Psi) e^{i\Delta} = r_p / r_s, \tag{1}$$

where r_p and r_s are the complex Fresnel reflection coefficients of the sample for *p*- (in the plane of incidence) and *s*- (perpendicular to the plane of incidence) polarized light. Spectroscopic ellipsometry (SE) measures the complex ratio ρ as a function of wavelength. Because ellipsometry measures a phase quantity "Δ" (as well as an amplitude ratio), it is highly sensitive even to the presence of films thinner than 1 nm.[12]

A commercial *in situ* SE system was used in this work. This system simultaneously acquires a complete spectrum of ellipsometric data at 88 wavelengths covering a 276–763 nm spectrum. The minimum acquisition time for a single spectrum is 1/25 s, but typical rates are 0.5–5 s. The angle of incidence was nominally 75°, and was determined accurately from the calibration procedure using a thermally oxidized silicon wafer with known optical constants.[13,14]

C. Oxygen plasma exposure

An ECR oxygen plasma chamber, as illustrated in Fig. 1, was used for exposure studies. Attached onto this chamber is an *in situ* ellipsometer that allows for real-time monitoring. The nominal power of the ECR was 60 W, the oxygen flux flow was 2 sccm, and the gas pressure in the chamber was in the 10^{-4} Torr range. The plasma volume was $\sim$190 cm^3. Materials were exposed to the oxygen plasma, which contains atomic oxygen, along with other charged and uncharged species. The equivalence between this plasma exposure and the erosion due to the LEO environment was determined by measuring Kapton weight loss.[15–17] It is well-known that atomic oxygen flux depends strongly on solar activity and position, the estimated constituent concentrations (5×10^9 atoms cm^{-3} at 200 km altitude above earth, and 5×10^5 atoms cm^{-3} at 600 km altitude) and the spacecraft velocity of $\sim$8 km s^{-1} give estimated oxygen–atom fluxes of 4×10^{15} oxygen atoms cm^{-2} s^{-1} at 200 km and 4×10^{12} cm^{-2} s^{-1} at 600 km. Typically, a space shuttle mission is flown at an altitude near 300 km, and a space station orbits the earth at $\sim$400–500 km altitude. Based on Kapton weight loss results, 1 hr of exposure time under current irradiation conditions corresponds to $\sim$96.4 days at 200 km or $\sim$264 years at 600 km in the actual LEO environment.[18]

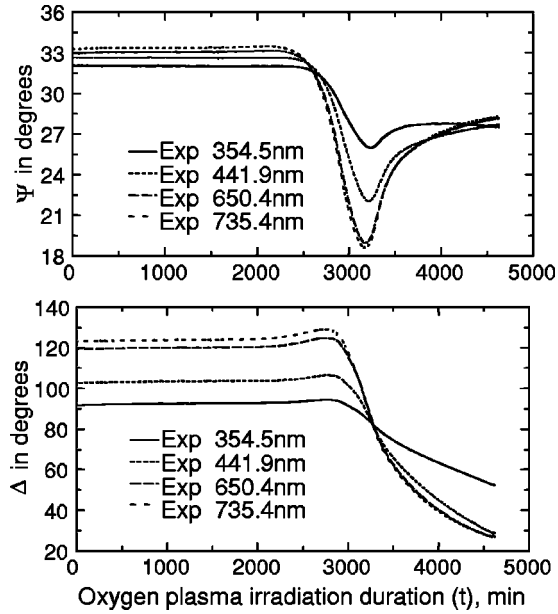


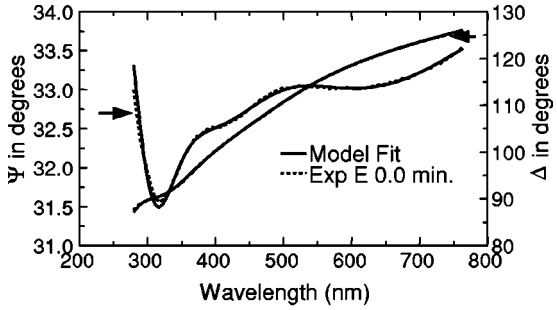
FIG. 2. *In situ* SE raw data during oxygen plasma irradiation of an iridium/chromium/fused silica substrate: (a) Ψ, (b) Δ.

III. RESULTS AND DISCUSSION

Figure 2 shows the real-time ellipsometric Ψ and Δ data taken from an Ir/Cr/fused silica substrate under oxygen plasma irradiation. For clarity of the graph, the separate lines represent data at 4 out of 88 available wavelengths. There are no changes detectable in Ψ or Δ until around 1700 min into the run, indicating that the iridium film remained optically thick for that long before it finally became transparent, and that the surface condition (roughness or oxidation) did not significantly change.

Prior to oxygen plasma irradiation, the roughness of the as-deposited iridium films were determined from AFM measurements, and the film optical constants were then determined accurately through regression fits to the SE raw data.[19] Details on the iridium film optical constant determination are described elsewhere.[9]

In this work, spectroscopic ellipsometric data were taken as a function of time, *t*, during plasma exposure (see Fig. 2). Shown in Fig. 3 are the SE data (at 88 wavelengths covering a 276–763 nm spectrum) at $t=0$ min, along with the regression fits based on the optical model shown below the graph. In this model, the iridium film optical response was represented by a classical Drude dispersion layer, along with seven Gaussian oscillators, to account for both free carrier and interband absorptions, respectively.[9] Surface roughness was modeled using a Bruggeman effective medium approximation (EMA) layer, using the rms thickness values taken directly from AFM results, assuming 50% iridium and 50% void. We realized that AFM and optical models may not yield the same values for roughness; however, they are closely related.[19] Because pristine Ir films were optically

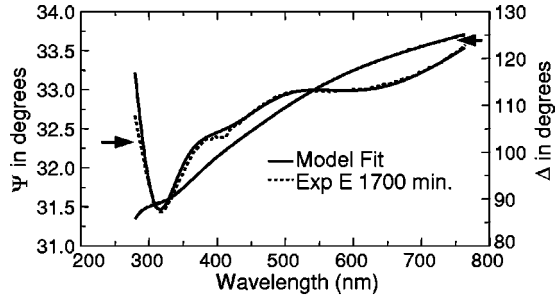


(a)

3	Roughness (EMA)	0.7 nm
2	Ir	240 nm
1	Cr	14 nm
0	Fused silica	1 mm

(b)

FIG. 3. (a) SE data at $t=0$ min along with the regression fits; (b) the optical model.



(a)

2	Roughness (EMA)	1.037 nm
1	Ir	58.037 nm
0	Fused silica	1 mm

(b)

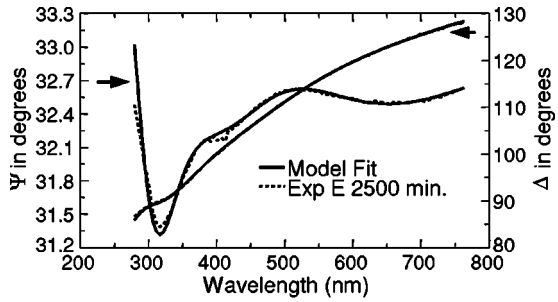
FIG. 4. (a) SE data at $t=1700$ min along with the regression fits; (b) the optical model.

thick, whatever layers are underneath (including Cr buffer and fused silica substrate) had no effect on the data at this time. The final as-determined iridium film optical constants were thus fixed in the subsequent regression fits as oxygen plasma irradiation progressed. The same surface roughness/iridium (optically thick)/chromium/fused silica model was valid for as long as the Ir film was opaque, which, under current exposure conditions, was found to be ~1700 min into the irradiation. During the first 1700 min, the iridium film remained optically thick and was represented by a thickness of 240 nm in the optical model. The roughness (EMA) layer thickness in the model changed only slightly, while showing no trends in time. The fit parameters during this period were (1) roughness layer thickness and (2) void percentage within the EMA layer. The use of void percentage as a variable allows for a more flexible and accurate representation of surface roughness. Despite the small fluctuation from time to time, the void percentage was found to be in the neighborhood of 57%.

Approximately 1700 min into the irradiation, the Ir film was no longer optically thick and light started reaching layers underneath. In addition to the surface layer (thickness and composition), the information carried by the SE data now may also include: (1) Ir layer thickness; (2) Cr layer thickness; and (3) oxidation and/or roughening. Shown in Fig. 4 are the SE data at $t=1700$ min, along with the regression fits based on the optical model shown below the graph. Two models were tried to account for the Ir surface layer, including graded layer[20] and EMA surface roughness. Both models worked reasonably well, with low MSEs; however, the differences were not significant enough to define a single unique model. Both models did, however, give similar results, namely the surface layer thickness was on the order of 1–2 nm.

Optical constants of chromium were measured in separate *in situ* experiments. However, the Cr buffer layer thickness was not resolvable from Ir. The reasons for this are: (1) At this stage of plasma irradiation, the Ir film was still too thick for significant light intensity to reach the layers underneath; and (2) the contrast between Ir and Cr optical constants is too weak for these two layers to have uncorrelated thicknesses.

From 1700 min and longer, the Ir film thickness was found to decrease gradually. By 2500 min into the run, penetration of the oxygen plasma through the thinner Ir film likely resulted in oxidation of the Cr buffer layer, and thus introduction of chromium oxide into the film stack. Shown in Fig. 5 are Ψ and Δ fits at $t=2500$ min based on the three-layer optical model shown below the graph. The EMA layer consisted of chromium oxide atomically mixed with Ir representing the oxide layer and whatever interface (or roughness) layers may actually be present. Optical constants of Cr_2O_3 were available[20] and used for convenience, not to imply the actual stoichiometry of the oxide. Judging from its thickness (43 nm), chromium oxidation must have started earlier; but until this point, the SE data were either unaffected by the films underneath ($t<1700$ min, when the Ir



(a)

3	Roughness (EMA)	1.211 nm
2	Ir	28.760 nm
1	EMA Ir/75.6% (Cr_2O_3)	43.339 nm
0	Fused silica	1 mm

(b)

FIG. 5. (a) SE data at $t=2500$ min along with the regression fits; (b) the optical model.

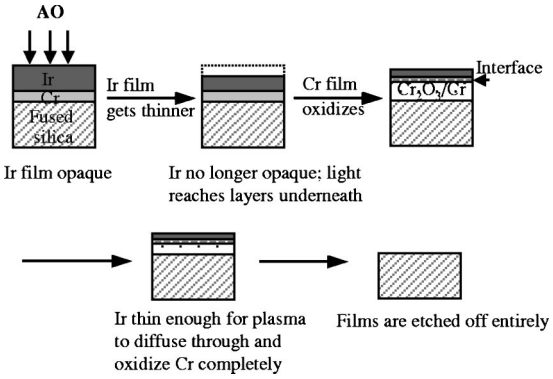


FIG. 6. Schematic of the plasma etching process.

film was optically thick) or not sensitive enough (t =1700–2500 min) to extract the oxide information with high confidence. Forty-three nm of chromium oxide is large, considering the considerable amount of Ir (28 nm) on top at this point. To form an oxide of that much thickness, chromium had to have been oxidizing since earlier stages ($t<2500$ min), when the Ir was still quite thick. Possible explanations are: (1) oxygen atoms diffused along Ir metal grain boundaries rather than through bulk, yielding a much greater diffusion rate; (2) etching was nonuniform and oxygen atoms diffused laterally. The light beam was large compared to film thickness, so the final determined thickness was a spatial average. One could argue that this EMA layer should also include Cr, because oxidation takes time, and the process is gradual. Physically, this is reasonable; but again, because of the aforementioned correlation between Ir and Cr optical constants, only one metallic component (Ir, in this case) was allowed in the EMA. Still, it should be kept in mind that, this EMA layer actually comprised three components: Ir, Cr, and chromium oxide.

A schematic diagram of this oxygen plasma etching process is given in Fig. 6. Essentially, it is a visual representation of the optical model results at different stages of plasma irradiation. The Ir film thickness was found to decrease gradually, as seen in Fig. 7, with an approximate etch rate of ~0.043 nm per minute. Approximately 2500 min later, the etching process slowed down slightly, indicating a decreasing etch rate. Points in Fig. 7 were from SE fit results at individual time slices. As a reminder, the Ir film thickness information was not available until ~1700 min into the run, when the film became partially transparent. Also shown in Fig. 7 are the chromium oxide (EMA) layer thickness and volume percentage within the EMA. It is interesting that these two parameters follow a "strange" pattern: They both start off decreasing and then ($t=\gtrsim 2750$ min) go back up again. Apart from Cr_2O_3, Cr has other oxidation states as well, including CrO_2, CrO_3, and Cr_3O_4. As mentioned previously, Cr_2O_3 was only chosen in our modeling because of the availability of its optical constants. The formation and/or interconversion of these oxides could have led to those downturns. The subsequent upturns, on the other hand, do make sense. As the etching of Ir continued, the Cr film underneath oxidized as well. By ~2750 min into the run, the pure Ir film on top of the chromium oxide layer was thin enough that the oxygen plasma could easily diffuse through and fully oxidize the Cr underneath. The remnant Cr oxidized completely in a relatively short period of time, giving rise to an increasing total layer thickness as well as an increasing chromium oxide percentage within the EMA. By 3000 min, the chromium oxide percentage had increased up to ~96%, which essentially corresponds to pure chromium oxide.

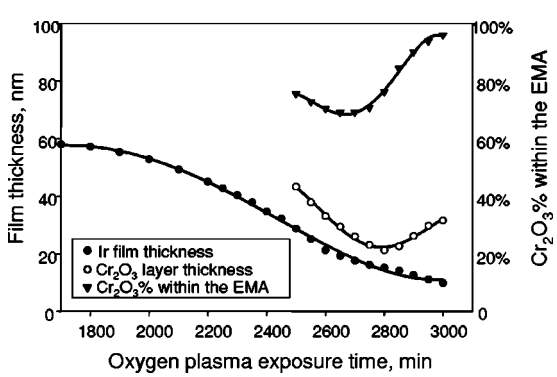


FIG. 7. Change of film thickness as well as composition vs oxygen plasma exposure time.

As the plasma etching continued with the Ir film getting thinner and thinner, the structure of the entire film stack became very complex. Various factors, such as surface roughness, film nonuniformity, and interfacial effects, etc., started mixing together, making modeling extremely challenging. Without an additional analytical technique, we were only able to fit the data through 3000 min into the run and even then, a patterned surface model needed to be introduced to account for lateral film nonuniformity. At this point, ~95% of the Ir was etched away. As the irradiation continued, eventually the Ir film, along with chromium oxide, was etched entirely off the area where the plasma was directed towards the sample surface. An empty spot was left behind, approximately the size of the plasma beam.

According to Kapton weight loss calibration,[18] 3000 min of irradiation time under current exposure condition corresponds to ~13.2 years at the lowest altitude in the LEO environment (200–700 km). As the altitude increases, so will the corresponding time in LEO for the same total exposed fluence. Generally, the corresponding duration for a spacecraft circling in the middle of LEO is on the order of 10^2–10^3 years. For iridium metal films to serve as substrates in space contamination studies, they have to have superb stability in the adverse environment in space for the duration of experimental studies. Technically, this means few or no detectable changes on the surface, physically or chemically, for a reasonable period of time compared to contamination study experiments, which at most might be a few years. In this work, the Ir film remained optically thick (opaque) until ~1700 min into the run, an equivalent of ~7.4 years at 200 km in the actual LEO environment. For higher altitudes, again, we would expect even longer periods of time (hundreds of years, on average). Note that, even as the iridium

film slowly etched, its surface quality (roughness) was minimally affected. This is also very important for contamination studies. The etch rate was found to be ~0.043 nm per minute in the laboratory plasma, or ~9.8 nm per year at the lowest altitude in LEO. Clearly, even 7.4 years of stable life in LEO is far more than necessary for iridium metals to be acceptable as substrates for contamination studies. Moreover, iridium films could be made thicker, taking even longer to become transparent. However, the tradeoff is that increasing film thickness increases surface roughness,[9] which is certainly not desired for substrates. The ultimate goal is to find a good balance between film thickness and surface roughness. Suffice it to say, iridium metal can indeed be used as substrates in space contamination studies.

IV. CONCLUSIONS

Ellipsometry, in simultaneous kinetic and spectroscopic mode, has been used to monitor oxygen plasma etching of iridium, a potential substrate for use in space contamination studies. Optical modeling performed at successive stages of the process has helped us gain a fundamental understanding of the plasma etching mechanism. Upon exposure the Cr buffer layer underneath was found to oxidize. As the plasma irradiation progressed, the Ir film became thinner, with an etch rate of ~0.043 nm per minute (or, ~9.8 nm per year at the lowest altitude in LEO). Approximately 1700 min of exposure time—an equivalent of ~7.4 years at 200 km altitude in space—was needed for the Ir film to become transparent. Late in the run ($t > \sim 3000$ min), the structure of the entire film stack became very complex and various factors started mixing together, making it virtually impossible to define a unique, physically reasonable optical model. However, the optical model versus exposure time progression presented in this paper worked reasonably well before and during complex microstructural changes taking place on a nanometer scale.

ACKNOWLEDGMENT

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