ABSTRACT

The present paper describes the changes in the structural and optical properties of the sputter deposited iridium films annealed in air and slow cooled from 673K-1073K. Glancing Angle X-ray Diffraction (GAXRD) and X-ray Reflectivity (XRR) measurements were used for the structural investigations of the films. GAXRD and X-ray reflectivity measurements showed growth of ∼4nm IrO2 over-layer by annealing at 873K. Increased annealing temperatures lead to the formation of oxidation of the iridium under-layer, with the film comprising iridium-oxide (major) and iridium (minor) phases. Increased surface roughness associated with the films annealed at 873K and 1073K was attributed to the growth of a crystalline IrO2 layer. Variable Angle Spectroscopic Ellipsometric (VASE) measurements in the wavelength range 300-1200nm, are presented for the as deposited iridium films and film annealed in air at 1073K. Estimated thickness of as-deposited iridium metal film was consistent with XRR results. The ellipsometry data for the annealed film was modeled using Lorentz oscillator layer. The results indicated the presence of conducting layer of Iridium oxide.

INTRODUCTION

Iridium metal is a promising candidate for a wide range of applications due to its chemical stability, high melting point, high mechanical strength, superior oxidation resistance and high electrical conductivity. Iridium metal has been investigated for its possible application as protective coatings on structural carbon materials [1], Re-rocket thrusters [2], heavy-metal-ion sensors [3], and patterned thin-film microelectrodes that interface to nervous tissue [4]. Iridium dioxide had been investigated for its potential application as the top layer electrode in Pb(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} (PZT) /Pt ferroelectric capacitors to suppress degradation [5], in high-density ferroelectric memories [6], oxygen stable electrodes in corrosive materials [7], and switching layer in electrochromic devices [8]. Various methods have been employed to prepare Ir [1-4, 9, 10,11] and IrO\textsubscript{2} [5,11-14] films.

Structural and transport properties of thin films can be controlled effectively by deposition conditions and post-deposition thermal and mechanical properties. Microstructure plays an important part in the physical, optical and mechanical properties of thin films [15]. We previously reported detailed x-ray analysis of Ir-IrO\textsubscript{2} films [16]. This paper reports the changes in the structural and optical properties of the sputter-deposited iridium films on Si substrates annealed in air at temperature 673K-1073K. GAXRD, XRR, Spectroscopic ellipsometry measurements in the wavelength range 300-1200 nm were used for characterization of the as deposited and annealed films.
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EXPERIMENTAL

Iridium metal films were sputter deposited on Si wafers in argon using an Ir target. The substrate temperature was held at ~723K and a deposition rate of 10-15 Å/s was utilized. The Ir metal films were heated in air at 673K, 873K and 1073K for 1hr and cooled in the furnace after the furnace was switched off. A Brüker D-8 Discover X-ray diffractometer with a goniometer having seven axes of motion and a Göbel Mirror on the primary beam side was used for the GAXRD and XRR studies. For GAXRD measurements, the angles of incidence were varied from 0.25-1.0° in increments of 0.25° and measurements were performed with soller slits (0.4° separation) on the secondary beam side. The peak separations have been analyzed by fitting with TOPAS-P software provided by Brüker [17]. XRR measurements using Knife-Edge Collimator (KEC) were setup to have a minimum of 1500 counts for the measurement range. The step size in XRR measurement was 0.003° in Theta. The multi-range data were normalized and the results were simulated using the REFSIM software (Brüker) [18].

Spectroscopic ellipsometric data were acquired using J.A.Woollam Company VASE® ellipsometer. Optical modeling and data analysis were done using the Woollam Company using WVASE32™ software package [19]. Ellipsometric data (ψ and Δ) were acquired at three angles of incidence (70°, 75° and 80°) over the spectral range 300-1200 nm in steps of 10nm. Multiple angle and wavelengths were fitted simultaneously in the optical models.

RESULTS AND DISCUSSION

GLANCING ANGLE XRD MEASUREMENTS

In thin film X-ray diffraction, signals from the layer can be maximized by carrying the measurements at fixed low glancing angles (α) of the primary beam. The sample can then be characterized as a function of depth by varying the angle of incidence angle of incidence between the critical angle of incidence (αc) for the total reflection of X-rays and ~1° [20-23].

The GAXRD measurements for 20 nm film as-deposited films are shown in Fig1a. The

![Figure 1. Glancing angle incidence x-ray diffraction patterns α = 0.5° and 1.0°, on 20 nm iridium films (a) as deposited (b) annealed at 873K and (c) 1073K for 1hr in air. Symbols (+) represent the reflections for Ir and (*) for IrO2 phases. Key Miller indices are indicated on the patterns](image)
measurements have been performed for 2-theta range 20-130°. Comparison of the relative intensities of the (111), (200), (220), (311), (222), (400), (311) and (420) diffraction peaks with the standard data for iridium [24] shows the presence of preferred orientation of the Ir planes along (111) reflection [9]. The GAXRD results for the sample annealed at 673K are similar to the as-deposited film with no Ir-IrO2 conversion on the surface.

Fig 1b shows the GAXRD results for the as-deposited film annealed at 873K. The XRD curve for $\alpha = 0.5$ shows the presence of the dominating IrO2 peaks. As $\alpha$ was increased to 1.0°, the contribution from the underlying layer of Ir metal increased and the Ir peaks dominated the XRD curve. The results indicate the presence of an overlying oxidized layer of Ir metal, as a consequence of annealing at 873K.

For the film annealed at 1073K, no change in the relative intensities of Ir and IrO2 phases was observed in the XRD spectra, as $\alpha$ was varied from 0.5° to 1.0°. Comparison of the area under peak for cubic Ir [111] and tetragonal IrO2 [110] indicated the presence of an IrO2 “major” phase and an Ir “minor” phase [14]. However, no attempt was made to quantify the phase fractions due to the finite thickness of film with respect to X-ray penetration. This is a reasonable estimate based on the basis of the physical and chemical nature of the films annealed at 1073 K. An increased annealing temperature of 1073K lead to the oxidation of the underlying Ir metal films, with the formation of islands of Ir metal being possible. Using Scherer’s method to analyze the (311) peak, excluding the instrument broadening effect, the crystallite size was estimated to be $\sim 2 \pm 1$ nm. The small size of the iridium crystallite was also evident by the extreme broadening of the (311) peak for the annealed sample, as compared to the iridium powder sample. Under the same measurement conditions full width half maximum, for the (311) reflection for the film annealed at 1073 K and standard powder sample were $\sim 1.0°$ and $\sim 0.16°$, respectively. The cubic iridium (311) reflection at $2\theta = 83.445°$ [24] was used for better signal to-noise ratio and also because the Ir (311) reflection does not have any overlapping reflection from the tetragonal IrO2 [25]. Comparison of the relative intensities of the diffraction peaks with the standard data for IrO2 [25] also indicates a preferred orientation along (110) plane. The results for the films annealed at 1073K are shown in Figure 1c. Finally our analysis did not reveal the formation of crystalline SiO2, a phase that could result from the reaction of air or IrO2 at the Ir, IrO2/Si interface.

X-RAY REFLECTIVITY MEASUREMENTS

The X-ray reflectivity involves the measurement of scattered intensity from the air-material interface near the critical angle of total external reflection. The plot of log of scattered intensity verses angle of incidence can then be modeled for the density, thickness and interface roughness for film and multi-layer [18, 26, 27].

Figure 2 shows the measured XRR spectra for the as-deposited and annealed films. The results for the simulated curve are tabulated in Table 1. As seen in the figure there is neither an appreciable change in the density of Ir film nor any formation of IrO2 over-layer from annealing the film at 673K since these films are nearly identical in their patterns. The XRR results could not be effectively simulated for the thickness of film for 1073K and the iridium under layer for 873K due to large surface/interface roughness. These results are consistent with the AFM studies
by earlier authors [14] where it had been observed that Ir metal films annealed at 873-1073K exhibit large rms roughness and surface height range. This increased roughness due to annealing had been attributed to the growth of IrO₂ crystalline structures [14]. However, the density values for film at 1073K and 873K could be estimated from the critical angle of incidence (\(\alpha_c\)) for the total external reflection of X-rays, above which the reflected intensity rapidly drops by several orders of magnitude [18, 26] using the relation [18]

\[
\alpha_c = \lambda (\rho)^{1/2} \times 1.64 \times 10^{-3}
\]

where \(\lambda\) is the wavelength of X-ray radiation and \(\rho\) the density of material.

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>Estimated Density (gm/cm³)</th>
<th>Thickness (nm)</th>
<th>Material</th>
<th>Theoretical density (gm/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>22.4±0.5</td>
<td>20.6±1.0</td>
<td>Ir</td>
<td>22.65</td>
</tr>
<tr>
<td>Annealed at 673K</td>
<td>22.4±0.5</td>
<td>20.4±1.0</td>
<td>Ir</td>
<td>22.65</td>
</tr>
<tr>
<td>Annealed at 873K</td>
<td>11.2±0.5</td>
<td>4.9±0.5</td>
<td>IrO₂</td>
<td>11.70</td>
</tr>
<tr>
<td></td>
<td>22.3±0.5</td>
<td>*</td>
<td>Ir</td>
<td>22.65</td>
</tr>
<tr>
<td>Annealed at 1073K</td>
<td>11.20±0.5</td>
<td>*</td>
<td>IrO₂</td>
<td>11.70</td>
</tr>
</tbody>
</table>

* Could not be simulated due large surface/interface roughness

### SPECTROSCOPIC ELLIPSOmetry MEASUREMENTS

Figure 3(a) shows the variation of ellipsometric data “\(\psi\)” as a function of wavelength and angle of incidence in wavelength range 250-1000nm for the as deposited Iridium film. The data was modeled using a standard iridium metal layer on Si wafer [19]. The thickness of the layer was estimated to be 21.4±1 nm, which is consistent with the XRR results. Inset in figure 3(a) shows the variation of refractive index “\(n\)” as a function of wavelength, obtained from the fitted results.
Figure 3(b) shows the spectroscopic ellipsometry spectra for the iridium films annealed in air at 1073K. The layer exhibits Drude-like strong IR-absorption that tails into the visible range [28]. The results are indicative of the presence of conductive iridium oxide layer, which are consistent with the observation by other authors [29,14]. The data was modeled using Lorentz oscillator model [19] using 2 of 7 available oscillators. The values for the oscillator parameters are given in Table 2.

While the GAXRD measurement does not indicate the presence of separate layer, the spectroscopic ellipsometry data could only be modeled using two layer structure. This may be due to graded Ir-IrO₂ layer [28]. However, the data could not be modeled completely for the analysis of microstructure due to high surface roughness, as indicated by the XRR measurements.

![Figure 3](image)

**Table 2**

Fitted oscillator parameters for the spectroscopic ellipsometry measurements on iridium film annealed in air at 1073K

<table>
<thead>
<tr>
<th></th>
<th>Thickness (nm)</th>
<th>Offset (ε₁∞)</th>
<th>Oscillator or Term #</th>
<th>Oscillator Amplitude (eV²)</th>
<th>Oscillator Broadening (eV)</th>
<th>Oscillator Energy position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Lorentz Oscillator Layer</td>
<td>57.431</td>
<td>1.4243</td>
<td>1 2</td>
<td>10.32 500.24</td>
<td>0.4181 6.6527</td>
<td>0.0224 9.1509</td>
</tr>
<tr>
<td>Bottom Lorentz Oscillator Layer</td>
<td>19.153</td>
<td>0.2028</td>
<td>1 2</td>
<td>0.29068 1.289</td>
<td>0.62398 0.7053</td>
<td>0 2.906</td>
</tr>
</tbody>
</table>
CONCLUSION

Annealing the as-deposited iridium film at 873K, leads to the formation of an IrO$_2$ over-layer accompanied by increased roughness. Further annealing at 1073K leads to the Ir-IrO$_2$ conversion, with the conducting film consisting of separate but intimate phases of IrO$_2$ (major phase) and Ir (minor-phase). Annealing of the iridium film in air at 1073K, led to the formation of small iridium crystallites (~2 nm) surrounded by the IrO$_2$ phase. Ellipsometry data indicates that the Ir-IrO$_2$ layer may be graded across the thickness. XPS measurements as a function of thickness indicate the presence of oxygen grading across the film thickness [16].

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