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# CHARACTERIZING CRYSTALLINE CHROMIUM OXIDE THIN FILM GROWTH PARAMETERS

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**Abstract.** Thin films of $Cr_xO_y$ were deposited on glass and stainless steel substrates at low temperature (< 500 °C). The films were prepared using a midfrequency (40 kHz) AC sputtering technique in an Isoflux ICM-10 sputter deposition system consisting of two hollow cylindrical targets of Cr in an argon-oxygen plasma. The effects of RF magnetron power, substrate biasing and the plasma's oxygen to argon ratio on the films' crystal orientation and hardness were investigated. The stoichiometric O/Cr ratio was determined from energy dispersive X-ray spectroscopy analyses. These studies gave a ratio of 1.5 when the argon to oxygen ratio was 1. When the steel substrates were biased at (-25 V) DC, the hardness nanoindentation test of the deposited films gave values up to 30 GPa. These values indicate growth of decidedly crystalline $\alpha$-$Cr_2O_3$ films on these substrates.

## 1. INTRODUCTION

Chromium oxides, $Cr_xO_y$, are of great interest due to the variety of their applications in a number of fields such as protective coatings for read-write heads in digital magnetic recording units, applications involving corrosion/oxidation resistance, and in glass blowing applications. The oxygen atoms in $\alpha$-$Cr_2O_3$ crystalline structure (rhombohedral) have an HCP arrangement which is known as the corundum structure. In general, chromium oxide can be deposited by various techniques, including thermal spray [1,2], chemical vapor deposition (CVD) [3], ion implantation [4], and physical vapor deposition (PVD) [5,6]. Results of these sputtering studies show that excess oxygen must be introduced during the deposition process to reach a film composition close to that of $Cr_2O_3$. Nevertheless, when the films exhibit an amorphous structure it can be crystallized upon appropriate annealing [6,7]. However, there were studies that showed $Cr_xO_y$ with O/Cr equals to 1.5 could be deposited directly by sputtering from a pure chromium target under carefully controlled deposition conditions [7]. The difficulty in obtaining stoichiometric $Cr_2O_3$ thin films is that there are a very large number of stable oxide phases of chromium. These stable phases include: CrO, $Cr_2O$, $CrO_2$, $Cr_2O_3$, $Cr_3O_4$, etc. During deposition, oxygen plays a major role in determining the crystalline phase in the film. Therefore, in order to get the alpha phase, the argon to oxygen gas flow ratios should be carefully controlled to obtain O/Cr stoichiometry of 1.5. The influence of oxygen's partial pressure and substrate biasing on the growth and properties of $Cr_xO_y$ thin films has been reported in literature [8,9]. It has been shown [8] that when the number of consumed oxygen atoms equals the sputtered chromium atoms the deposition process moves from metallic to reactive. However, this one to one

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**Table 1.** Deposition parameters.

| Sample number | Power (kw) | Argon (sccm) | Oxygen (sccm) | Ar:$O_2$ | Bias (V) | Substrate |
|---|---|---|---|---|---|---|
| 1 | 4 | 45 | 45 | 3:3 | 0 | Glass |
| 2 | 5 | 45 | 45 | 3:3 | 0 | Glass |
| 3 | 6 | 45 | 45 | 3:3 | 0 | Glass |
| 4 | 5 | 60 | 45 | 4:3 | 0 | Glass |
| 5 | 5 | 30 | 45 | 2:3 | 0 | Glass |
| 6 | 5 | 45 | 45 | 3:3 | -25 | Stainless Steel |

ratio correspondence causes target poising and therefore reduces the deposition rates. Harder films have a O/Cr ratio which is very close to 1.5; therefore this property could be crudely implemented in checking the stoichiometric ratio. The effect of oxygen partial pressure on the hardness of $\alpha$-$Cr_2O_3$ thin films was studied by Hones *et al.* [10]. The results showed, for a low oxygen partial pressure (between 15-20%), the films exhibited higher hardness without any development of residual stresses which is typical for the alpha phase chromium oxide.

In the present study, $Cr_xO_y$ thin films were deposited on glass and stainless steel substrates using a midfrequency (40 kHz) AC sputtering Isoflux ICM-10 system. The effect of magnetron RF power, substrate biasing and the plasma's argon to oxygen ratio on the films' crystal growth and hardness properties was investigated.

## 2. EXPERIMENTAL

The $Cr_xO_y$ films were deposited using an ac inverted cylindrical magnetron sputtering technique manufactured by Isoflux Inc. Two cylindrical plasma sprayed chromium targets (99.0% pure) were used to deposit the films. Argon (99.99 % pure) and oxygen (99.99 % pure) were used as the sputter and reactive gases, respectively. Glass and stainless steel were used as substrates. Before deposition, the samples were ultrasonically cleaned in isopropanol for 10 minutes. A (–25) V was applied to the stainless steel samples during deposition. The deposition temperature was determined to range from 350 °C at 4 kW to 480 °C at 6 kW using temperature sensitive paints [11]. The system was pumped to a base pressure of $1\times10^{-3}$ Pa and argon was introduced to initiate sputtering at $2.6\times10^{-1}$ Pa. The dimensions of the circular targets were 33 cm in diameter and 9.8 in height. These targets were powered simultaneously by an advanced energy (model PE II) power supply operated at equally spaced variable levels starting from 4 kW (20 kW/$m^2$) and ending with 6 kW (30 kW/$m^2$). More details of the sputtering system are given elsewhere [12]. The argon to oxygen ratio was changed at each operating

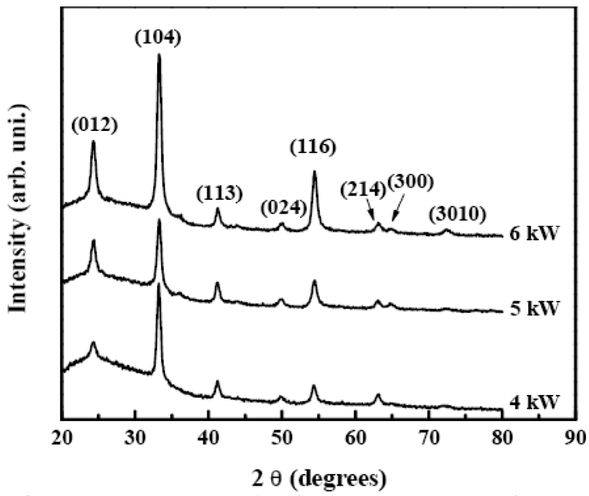


**Fig. 1**. XRD patterns for the glass samples deposited at different RF powers and a constant argon to oxygen ratio of 1.

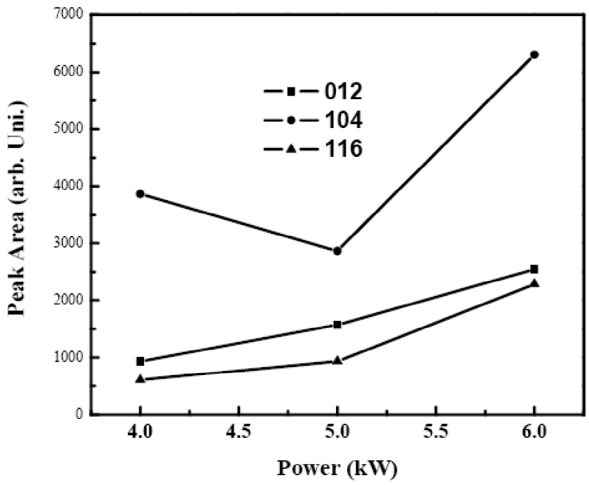


**Fig. 2**. Peak area as a function of RF power for different crystal planes.

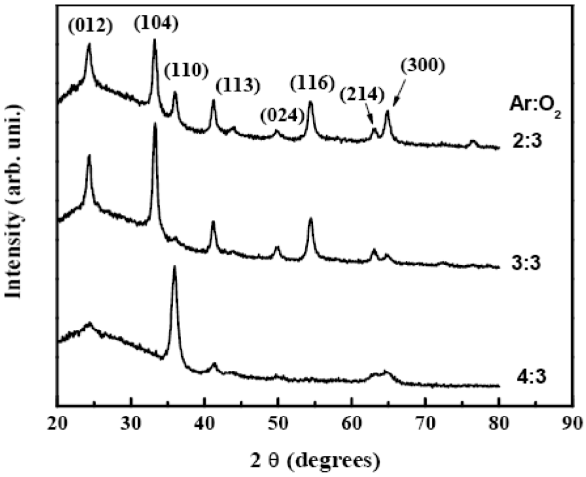


**Fig. 3**. XRD patterns for the glass samples at different argon to oxygen flow rate ratio.

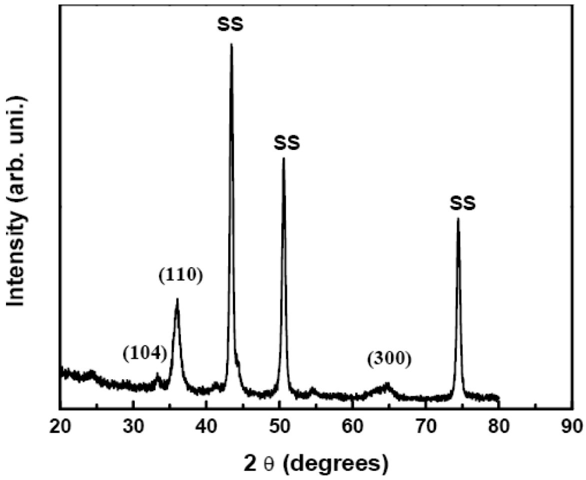


**Fig. 4**. XRD patterns for the steel samples. Three peaks for the oxide could be identified. The RF power was kept at 5 kW and the argon to oxygen ratio was 1:1.

power level. The deposition time for all films was one hour resulting in films about 0.5 microns thick [12]. A summary of all deposition parameters is given in Table 1.

X-ray diffraction (XRD) (Philips PW 1830) was used to determine the samples crystal structure and plane orientation. Scanning electron microscope (SEM) (Philips FEI XL 30) was used to observe the films' morphology. This system was used also to determine the elemental compositions of the films through energy dispersive X-Ray spectroscopy (EDX) analysis. The films' hardness was measured using a Micro-materials nanoindentation system.

## 3. RESULTS AND DISCUSSIONS

The deposited $Cr_xO_y$ films had a dark green color and showed good adhesion to the glass and stainless steel substrates. Fig. 1 shows the XRD pattern of the films deposited on the glass samples at constant argon to oxygen flow rate ratio. No shift in the peaks was observed with increasing RF powers. This pattern stability indicates that RF power plays minor role in determining any preferred crystal orientation in the films. However, the relative peak intensities appeared to change with increasing RF power as detailed next.

Fig. 2 shows the behavior of three different peaks shown in Fig. 1 as a function of the applied RF power. It is noted that the (104) peak intensity decreases with the intermediate RF power, whereas the other peaks intensity increased monotonically. These changes could be due to residual stresses created during deposition at this RF power. However, as the RF power increases, the atoms become more mobile on the film's surface as a result of higher bombardment rates on them. This added mobility to the films atoms helps the films to release stress and therefore more crystallization is possible. On the other hand, at lower RF power, the lower deposition rates helps in creating films with lower internal stress. Therefore preferential film orientations will grow more easily which can be observed for the (104) planes.

Fig. 3 shows the XRD results for the glass samples coated at different argon to oxygen flow rate ratios. The sputtering power in these runs was maintained at 5 kW. The samples with the 4:3 argon to oxygen ratio showed peaks corresponding to bcc metallic chromium with some oxygen incorporated in the lattice. This metallic structure did not show any unique phase of crystalline oxide. The 3:3 argon to oxygen ratio samples showed some signatures of alpha phase along with other crystalline phases. A single phase $\alpha$-$Cr_2O_3$ was observed along with higher oxides for the 2:3 argon to oxygen ratio. The excess oxygen in this case allowed the films to be deposited with lower internal stress resulting in lower internal energy. Therefore, the films retained the stable alpha phase crystalline structure.

Fig. 4 shows the XRD results for the films prepared on steel at 5 kW with an argon to oxygen flow rate ratio of 3:3. To study the effect of biasing on these samples, a DC bias of (-25 V) was applied

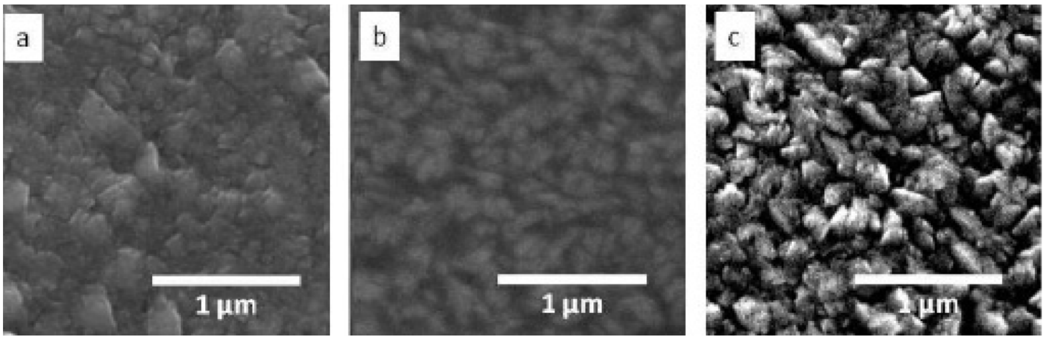


**Fig. 5.** SEM image of the glass samples at different argon to oxygen ratios. a) 2:3, b) 3:3 and c) 4:3. RF power was kept at 5 kW.

**Table 2.** The O/Cr ratio in the deposited films for different argon to oxygen flow.

| Ar:O | 4 KW | 5 KW | 6 KW |
|---|---|---|---|
| 2:3 | 1.8 | 1.9 | 1.9 |
| 3:3 | 1.5 | 1.5 | 1.6 |
| 4:3 | 1.2 | 1.2 | 1.3 |

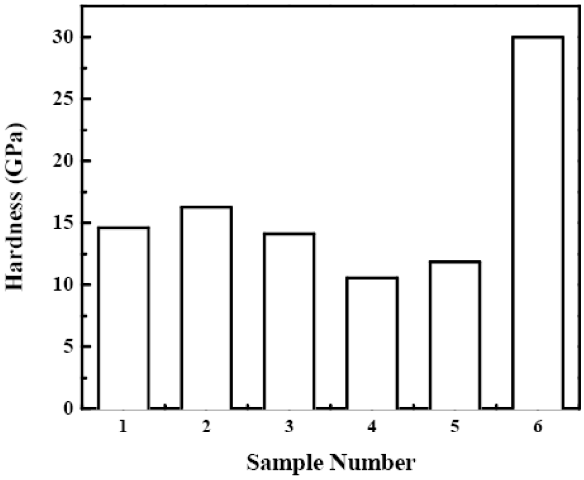


**Fig. 6**: Hardness values for the six samples. Sample number 6 which was biased at -25 V showed the highest hardness at 30 GPa.

during deposition. The XRD pattern showed a preferred (110) peak along with steel peaks. Although this preferred crystal orientation in the deposited films could be due partly to the substrate surface, we believe that this preferential orientation is because of the applied bias. Several reports [10-14] had indicated this conclusion this conclusion. For example, Wang *et al.* [13] observed a (006) preferred orientation on steel substrates when (-70 V) was applied during film deposition. Substrate biasing affects the ion/metal flux ratio in the plasma during deposition. Adibi *et al*. [14] studied the effect of this parameter as well as the ion energy during deposition on the microstructure and crystal orientation of deposited films. In the case of reactive sputtering, they concluded that a variation in surface chemistry due to biasing which affects surface energy leads to a specific preferred crystal orientation. As a result of this interplay, only certain favorable oriented grains will survive and grow. Another example comes from the work of Schneider *et a*l. [15] were they controlled the growth of (300) planes of chromia-alumina films on a biased stainless steel substrates during reactive sputtering.

Fig. 5 shows the SEM images of the deposited films on glass at different argon to oxygen flow rate ratios. The power was kept at 5 kW in these samples. The film showed randomly oriented facets that are typical for a polycrystalline film. However, the surface morphology in these images indicated different feature sizes which could be due to different crystal orientations as indicated by the XRD patterns.

Table 2 shows the oxygen to chromium O/Cr ratio in the deposited films as determined from the EDX analysis at different argon to oxygen flow rate ratios and RF powers. The O/Cr ratio was determined by dividing the oxygen peak intensity (as measured from the EDX pattern) by the intensity of the chromium peak intensity (as measured also from the EDX pattern). It is noted here that at lower argon flow rates the films had higher oxygen content which is consistent with the XRD patterns (Fig. 3). The pattern indicates more crystalline peaks which could be due to several phases of oxide structures. On the other hand, films deposited argon to oxygen ration of 1 showed stoichiometric ratios of 1.5 within an experimental error of 0.2 as determined from the calculated standard deviation.

This stoichiometric ratio remains almost constant with RF power. At higher argon flow rates the films are more metallic. However, these films tend to become more stoichiometric with increasing RF Power.

Fig. 6 shows the hardness values as measured by nanoindentation for the six samples. The indents were made up to 10% of the film thickness to avoid the effect of substrate hardness. The first three films on glass (Samples 1, 2, and 3), with an equal argon and oxygen flow rate, recorded hardness values of 14.6, 16.2, 14.1 GPa, respectively. Sample 4 (also on glass) was deposited at a lower argon flow rate and recorded a lower hardness value (10.6 GPa) than did Sample 5 (11.8 GPa) which was again on glass but had a higher argon flow rate. Both of these values are lower than either of the first three samples. These low values may be due to poor adhesion on the glass substrates or nonstoichiometric coatings. In the case of Sample 5, the oxygen flow rate was higher than argon so the lower hardiness could be attributed to the incorporation of oxygen in the lattice which reduced the hardness closer to the metallic chromium. Furthermore, all films on the glass samples had cracks around the indents. On the other hand, hardness measurements on Sample 6 with stainless steel substrates showed a high value of 30 GPa.

The hardness of crystalline chromium oxide as reported in the literature is very close to this value [10]. Biasing increases the ion bombardment rate on the substrate film. Therefore the films will be less internal stress as mentioned above and they will also have finer, denser structure which will lead to higher hardness.

## 4. CONCLUSION

Thin films of $Cr_xO_y$ were deposited by AC inverted cylindrical magnetron sputtering technique at temperatures under 500 °C. It has been shown that the films' crystal orientation in reactive sputtering is affected by the RF power used, substrate biasing and the plasma's argon to oxygen ratio. Films deposited at higher oxygen flow rates had bcc metallic chromium with oxygen incorporated in the lattice. Films with equal flow rates showed $\alpha$-Cr2O3 crystalline structure along with other phases and exhibited O/Cr stoichiometric ratio of 1.5. The films deposited on steel substrates had a preferred crystal plane orientation in the (110) direction with (-25V) bias. The films' hardness on the steel samples was as high as 30 GPa as compared to much lower values for those on glass. Further investigation on the substrate film adhesion and its effect on the film hardness are desired.

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