Low-temperature deposition and hardness enhancement of α-(Al,Cr)\(_2\)O\(_3\) films by reactive high power pulsed magnetron sputtering

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**Abstract**

This paper offers a method to grow corundum structure thin films of α-(Al,Cr)\(_2\)O\(_3\) in a High Power Pulsed Magnetron Sputtering (HPPMS) system. The films were characterized by grazing incidence x-ray diffraction (GIXRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and nanoindentation. The results indicate that stoichiometric α-(Al,Cr)\(_2\)O\(_3\) film could be deposited at 540 °C without the formation of other metastable phases. The stable process of the magnetron sputtering ensures the smooth and compact surface of the film composed of nano-scale particles. The Cr in films can induce the formation of solid solution and enhance the mechanical property of the films. The hardness of the α-(Al,Cr)\(_2\)O\(_3\) was calculated as ∼ 25.6 GPa, which is much higher than that of the film deposited using the Al target. These results are considered have positive effect on the low-cost depositing α-phase alumina films on high speed steel substrates as cutting tools.

**1. Introduction**

Crystalline α-alumina (α-Al\(_2\)O\(_3\)) thin films are extensively used as wear-resistant, diffusion barrier and cutting tool coatings due to the superior performance of high hardness, wear and corrosion resistance, thermal and chemical stability [1–3]. For a long time, α-alumina films have been synthesized by chemical vapor deposition (CVD) in industrial scale, which requires a high deposition temperature above 1000 °C [4]. However, the high temperature not only limits the choice of substrate materials, but also results in some negative effects such as chemical reactions [5] or thermal cracks between the film and substrate [6]. Consequently, many studies on decreasing the deposition temperature of the alumina films have been approached during the last decade. Techniques such as pulsed plasma-assisted CVD [7] and some physical vapor deposition (PVD) methods [8] have been performed at low temperature while the metastable γ-, κ-, δ-, η- or θ-phases are generally present in the films [9–12], which may lead to a deterioration of the properties.

Growth of the films composed of dominating thermodynamically stable α-phase have been achieved at temperatures lower than 800 °C by several methods with high ionization proportion. Zywitzki et al [13] reported that the α-Al\(_2\)O\(_3\) could be deposited by pulsed direct current reactive magnetron sputtering at 760 °C. Wallin et al [14] obtained the α-Al\(_2\)O\(_3\) films at 650 °C by high power pulsed magnetron sputtering. Krylyov et al [15] successfully decreased the deposition temperature to 580 °C using the plasma assisted CVD. Unfortunately, considering the tempering temperature of the high-speed steel (lower than 560 °C), which are widely used as cutting tools in industrial manufacture, it is still too high for the application of this potential film material.

The deposition temperature of the α-Al\(_2\)O\(_3\) films could be lower by manipulating the substrate surface in order to promote the nucleation of α phase, which is mainly caused by the template effect [16, 17]. Both α-Al\(_2\)O\(_3\) and α-Cr\(_2\)O\(_3\) have the same corundum-type structure, similar mechanical properties and lattice constants...
(α-Cr2O3 crystallizes into the same hexagonal structure as α-Al2O3, with a lattice mismatch of 4.1% in the a- and 4.7% in the c-parameter). In contrast, α-Cr2O3 can be obtained more easily at low temperature (300 °C ~ 500 °C). Thus, the isostructural α-Cr2O3 has been considered as the ideal template material [18]. Furthermore, introducing the corundum-type seeds into the films during the deposition process can also decrease the temperature of the synthesis of α phase to a relatively low level. Pohler et al [19] prepared the α-(Al0.7,Cr0.3)2O3 films on a (Al0.25,Cr0.75)2O3 template layer at 350 °C. The same temperature was achieved by Qiu et al [20] in a radio frequency magnetron sputtering system and the Al-rich α-(Al0.7,Cr0.3)2O3 films were obtained by sputtering the Al–Cr alloy targets. Pedersen et al [21] reported that the solid solution α-(Al,Cr)2O3 films could grow on the α-Cr2O3 layers at 450 °C and the hardness of the films were in the range 24 ~ 27 GPa. Gao et al [22] prepared the α-(Cr1−xAl)x2O3 thin films (0.08 ≤ x ≤ 0.16) at 400 °C by co-sputtering the Cr2O3 and (Cr0.8Al0.2)2O3 targets. However, the utilization of the template interlayer complicates the process and the high content of α-Cr2O3 may reduce the thermal stability of the films. Therefore, there is still a need to develop an effective method for low-temperature deposition of α-Al2O3 films.

In our previous work [23], the complete solid solution α-(Al0.7,Cr0.3)2O3 film was deposited from the Al–Cr target at 550 °C by radio frequency magnetron sputtering. However, the deposition rate in the RFMS system was at a relatively low level and the deposition temperature can be further increased. This work aimed to demonstrate an approach to synthesize α-phase alumina films at lower temperature due to the combined effect of the template and the technique with high ionization proportion. Thus, the alumina and α-(Al,Cr)2O3 films have been deposited directly on Si(100) substrates by reactive HPPMS at 540 °C with the Al and Al–Cr targets. The phase structure and the mechanical properties of the films were compared to each other. The influence of the Cr content and the deposition progress were finally investigated.

2. Experimental details

2.1. Deposited by HPPMS

The thin films were deposited by reactive HPPMS in a sealed chamber with high vacuum. Sputtering were carried out from the Al (99.99% purity) and Al70Cr30 (99.95% purity) targets mounted on an off-axis single-cathode planar magnetron (diameter 60 mm). The Si (100) substrates were placed on a resistive heater directly above the magnetron at a target-to-substrate distance of 6 cm. Before deposition, the residual gas pressure was lower than 4 × 10−5 Pa and the Al70Cr30 and Al targets were pre-sputtered for 15 min at a 99.99% pure Ar atmosphere with a pressure of 1.0 Pa. For this process, the peak power was 5 kW (~180 W cm−2) and the average power was fixed at 150 W (~5 W cm−2), while the flow rate of Ar was kept constant at 24 sccm. Afterwards, the reactive O2 gas was injected and the flow rate was 1.9 sccm. The work pressure was modified at 0.5 Pa and the substrate temperature was 540 °C. For all depositions, the average power was set as 260 W (~9 W cm−2) with the duty cycle of 2.5%. To obtain the sufficient thickness for the nano-indentation tests, the depositions were performed for 180 min.

2.2. Characterization techniques

Grazing incidence x-ray diffraction (GIXRD) with Cu Kα-radiation was used to identify the phase structure of the films. The incident beam angle was 2° and the diffraction data were collected over a range of 2θ = 25 ~ 75° with a step width of 0.04°. The field-emission scanning electron microscopy (SEM) (Nova Nano SEM 430, Netherlands FEI) equipped with x-ray Energy Dispersive Spectroscopy (EDS) was employed to determine the microtopography and the thickness of the films using secondary electron mode. The resolution of this SEM is 1.0 nm at 15 kV. In addition, the elemental compositions were analyzed quantitatively by EDS method using back-scattered electron mode. The details of the microstructure were studied by the transmission electron microscopy (TEM) in a JEOL JEM-2100F equipment. To evaluate the nano-hardness and elastic modulus, nano-indentation tests were performed in a Hysitron TI 950 triboindentor and the calculated values were based on the theory of Oliver and Pharr [24].

3. Results and discussion

Figure 1 shows the GIXRD pattern of the films deposited with Al70Cr30 and Al targets (hereafter named sample I and II, respectively). Dominant peaks of α-Al2O3 (012), (104), (006) with minor peaks of α-Cr2O3 (110) and SiO2 (104), (204) have been detected in sample I. Excluding the SiO2, induced by the oxide layer of Si substrate, it indicates the formation of polycrystalline α-Al2O3 and α-Cr2O3 with lower content. The α-Cr2O3 plays a dominant role in the absence of the metastable phases in the film deposited with Al70Cr30 target. Since the crystalline α-Cr2O3 has the same corundum-type structure as α-Al2O3, the template effect of α-Cr2O3 promotes the nucleation of α-Al2O3 and inhibits the formation of metastable alumina [17, 25]. Crystalline α-Al2O3
nucleates on the surface of $\alpha$-Cr$_2$O$_3$ seeds, then the interdiffusion of the Al$^{3+}$ and Cr$^{3+}$ ions along the interface with high Gibbs free energy might result in the formation of partial solid solution $\alpha$-(Al,Cr)$_2$O$_3$ with higher stability [26]. Nevertheless, this interdiffusion of the metallic ions may not be quite sufficient due to the relatively higher deposition rate and lower substrate temperature (compared to those of the RFMS method [23]), which makes the formation of solid solution may only occur partially along the grain boundaries. Thus, the content of the solid solution might be relatively low and the unchanged diffraction angle $2\theta$ compared to $\alpha$-Al$_2$O$_3$ demonstrates the formation of substitutional solid solution $\alpha$-(Al,Cr)$_2$O$_3$ while the difference of atomic size may be adjusted by the slight torsion of the interstice. Moreover, the size of the nano-scale grains was calculated as 21 nm by Scherrer formula based on the full width at half maxima (FWHM) of diffraction peaks. However, more crystal phases have been detected in the film deposited with Al target as depicted in figure 1. Apart from the SiO$_2$ interference phase and strong peaks of $\alpha$-Al$_2$O$_3$ (012), (104), (006) and (116), crystalline Al (111), (200), (202) peaks are present as well. The appearance of biased (116) peak indicates a preferred orientation of the crystallites, as compared to the standard reference. The absence of the metastable phases, such as $\gamma$- or $\kappa$-Al$_2$O$_3$, can mainly be attributed to deposition process with high ionization proportion. The non-neglectable Al in sample II is mostly ascribed to the unstable deposition process performed using the Al target, which will be described in the subsequent part.

The content of the targets also plays an important role in the deposition process, which determines the microscopic quality of the films. Figures 2(a) and (b) demonstrate the surface and cross-section (inset) SEM micrograph of the films deposited with Al$_{70}$Cr$_{30}$ and Al targets, respectively. Sample I presents smooth, compact, crack-free structure and granular grains with the average size of around 20 nm, which is consistent with the value calculated by Scherrer formula. Nevertheless, sample II exhibits rough, microporous structure and inhomogeneous grains with the existence of large droplet due to the target poisoning. The average deposition rate of sample I was calculated as $\sim$2.94 nm min$^{-1}$ while sample II grew with the rate of $\sim$3.84 nm min$^{-1}$. The sputtering and deposition process of the film were sustained and stable during the preparation when the Al$_{70}$Cr$_{30}$ alloy was used as target. In contrast, the drastic hysteresis effect during the sputtering made the deposition process unstable, and the deep poisoning let to the spark on the surface of the Al target with a frequency above 3000 times per minute. These negative effects on the growth resulted in poor qualities of the film: on one hand, the ejection of droplets with size of several micrometers from Al target led to porous and rough structure which increased the thickness of films; on the other hand, the shielding effect of the droplets results in the presence of residual Al, as proved in figure 1.

Further EDS investigation on the elemental composition of the films are shown in figures 2(c) and (d). Carbon and silicon were introduced from the pollution in the atmospheric environment and the substrates, respectively. For Al$_2$O$_3$ and Cr$_2$O$_3$ crystals, stoichiometric ratios of the O atoms versus the metallic element are 1.5. Removing the influence of the interference elements, sample I possesses the atomic ratio of O/Al = 1.49, which nearly reaches the theoretical value and confirms the formation of stoichiometric (Al,Cr)$_2$O$_3$ in the film. However, the atomic ratio of O/Al = 1.43 for sample II is relatively lower. Taking the XRD results into account, the existence of residual aluminum which developed from the droplets and failed to react with the O$_2$ results in a film with improper contents.

More information on the microstructure of the film deposited with the Al$_{70}$Cr$_{30}$ target were characterized by TEM technique and the images are given in figure 3. It can be observed from figure 3(a) that the film is composed of nano-scale grains with the size of around 20 nm. The selected area electron diffraction (SAED) in figure 3(b) only exhibits corundum structures. According to the phase composition of sample I shown in figure 1, these...
diffraction rings can all be assigned to the mixture of $\alpha$-phase Al$_2$O$_3$ and Cr$_2$O$_3$. The standard references are marked as white dots and blue rings for the $\alpha$-Al$_2$O$_3$ and $\alpha$-Cr$_2$O$_3$ phases, respectively. However, it can barely distinguish between the rings from $\alpha$-Al$_2$O$_3$ and $\alpha$-Cr$_2$O$_3$ since the lattice parameters of these two crystals are extremely similar to each other. The high-resolution transmission electron microscopy (HRTEM) image (see figure 3(c)) of the film demonstrates three grains separated by the grain boundaries. The enlarged image gives more details on the interplanar spacing and angle so that the planes of $\alpha$-Al$_2$O$_3$ can be distinguished from those of $\alpha$-Cr$_2$O$_3$. The spacing of $\sim$2.20 Å and 1.93 Å in the left grain can be identified as the (105) and (106) planes of $\alpha$-Al$_2$O$_3$, which can also be confirmed by the fast Fourier transform (FFT) patterns shown in the boxed region. The right grain exhibits a set of slightly larger spacing of $\sim$2.78 Å and 2.00 Å, corresponding to the (105) and (106) planes of $\alpha$-Cr$_2$O$_3$. The FFT patterns in the right boxed region presents the (105), (201) and (106) planes of $\alpha$-Cr$_2$O$_3$ as well. On the contrary, the existence of the metastable phases can hardly be detected from the TEM images, which shows good consistency with the phase composition determined by GIXRD (see figure 1). The TEM analysis for sample II was performed under inappropriate condition due to the poor quality of the film deposited with Al target and the results of this film were considered lack of comparability, which are not shown here.

The mechanical properties were measured by nanoindentation with a constant Poisson’s ratio of 0.27 and the load versus displacement curves of the films are shown in figure 4. Sample I displays a relatively smaller displacement than sample II for the same load and five indentations were employed for each sample. The average values of nano-hardness were calculated as $25.6 \pm 3.2$ GPa and $17.1 \pm 1.9$ GPa for sample I and II, respectively, and the related parameters were given in the inset table. For both samples, the indentation depths correspond to 9% of the film thickness. The larger $H^2/E^2$ ratio for sample I indicates better resistance against plastic deformation than sample II [27]. Similar results can be obtained according to the values of Young’s Modulus. The enhancement of hardness and stiffness of sample I might be owing to two reasons. Firstly, the quite distinct sputtering process played the most important role in the mechanical property of the film. The target poisoning was alleviated and the sparking was suppressed by using the Al$_{70}$Cr$_{30}$ target, which made the deposition process stable and increased the compactness and surface quality of sample I. On the contrary, the relatively unstable process of sample II induced the occurrence of holes and droplets in the film and reduced the mechanical property of the film. Secondly, the formation of solid solution $\alpha$-(Al,Cr)$_2$O$_3$ along the grain boundaries in the film might also have an positive effect on the hardness. Considering the hardness of $\sim$22 GPa for the $\alpha$-Al$_2$O$_3$ film deposited by magnetron sputtering [28] and the similar hardness between the $\alpha$-Cr$_2$O$_3$ and $\alpha$-Al$_2$O$_3$,
Figure 3. TEM micrograph of the film deposited with Al70Cr30 target: (a) the low magnification cross-sectional morphology, (b) the SAED and (c) the HRTEM image of the film.

Figure 4. Load–displacement curves of the films.
sample I exhibits higher hardness of ~25.6 GPa which might partially be ascribed to the solution strengthening. Moreover, the solution could increase the degree of lattice distortion and density of dislocation, which determine the resistance against plastic deformation.

4. Conclusions

Thin film samples were deposited with Al70Cr30 and Al targets in a HPPMS system. The phase composition, microstructure, surface morphology and mechanical properties of the films were investigated. The film prepared with Al70Cr30 target have a preferable performance in sputtering process and mechanical property than that with Al target. The pure α-phase (Al,Cr)2O3 film with a hardness of ~25.6 GPa can be synthesized at a temperature of 540 °C, which is lower than the tempering temperature of high-speed steel. Thus, this work provides a practical and low-cost approach to deposit α-phase alumina films with stable reactive sputtering technics.

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