Effects of corundum-structured seeds on the low-temperature growth and hardness of the alumina-based films

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Abstract

The corundum-structured seeds have been introduced into alumina films using Al + α-Al₂O₃ composite and Al₁₀₀−ₓCrₓ (x = 10, 20, 30) alloy as targets by reactive magnetron sputtering. The effects of the seeds on the elemental composition, phase composition, structure characteristic, surface morphology and nano-hardness of the alumina-based films have been investigated. The Al target has also been sputtered to prepare the alumina film as reference. The film is composed of single-phase α-Al₂O₃ by sputtering the Al + α-Al₂O₃ composite target at 550 °C, while the solid solution α-type (Al₀.₇Cr₀.₃)₂O₃ was detected in the film prepared with the Al₇₀Cr₃₀ target at the same temperature. The nano-hardness of the pure α-Al₂O₃ film and the α-(Al₀.₇Cr₀.₃)₂O₃ film were measured as ~23.5 GPa and ~28.5 GPa, respectively, which are much higher than that of the film deposited from Al target (~16.3 GPa).

1. Introduction

Corundum-structured alumina (α-Al₂O₃) films exhibit great physical and chemical properties including high hardnness, good oxidation resistance, high physical and chemical stability. These properties make them one of the most attractive candidates for diffusion barrier, wear resistance and anti-oxidization coatings [1–3]. However, most of the polymorphs such as γ, κ or amorphous phases can hardly meet the requirements for these high-temperature applications [4–8], and only the corundum-structured α phase is considered thermodynamically stable. In commercial scale α-Al₂O₃ films have been synthesized by chemical vapor deposition (CVD) at a high substrate temperature of over 1000 °C [9], where the high cost cemented carbide is one of the few suitable substrate materials and some unwanted reactions between the film and substrate material might occur. Unfortunately, the metastable phases have a great change of being present in the film deposited at relatively low temperature, which will transform into the α-Al₂O₃ irreversibly at high temperature and lead to a relatively huge volume decrease associated to the cracking and failure [4]. Therefore, decreasing the deposition temperature of the high purity α-Al₂O₃ film is the crucial objective for expanding its practical applications.

Various methods have been performed to realize the low temperature growth of the α-Al₂O₃ films and the physical vapor deposition (PVD) is the priority for many researchers. According to the progressive work reported in last years, two types of experimental approaches have been performed [10]: one approach benefits from the high ionization proportion and energetic ion bombardment by using new pulsed plasma technologies or highly ionized PVD processes. Zywitzki et al.[11, 12] reported that films exhibited single α phase when deposited at a temperature higher than 760 °C in a pulse magnetron sputtering system. Selinder et al.[13, 14] successfully reduced the deposition temperature to 650 °C by using reactive high-power impulse magnetron sputtering (HIPIMS). The same low temperature was also achieved by Brill et al’s research [15], in which α-Al₂O₃ films were obtained in a filtered arc device with high substrate bias voltage of −300 V. A lower temperature of 560 °C for the α-Al₂O₃ films was reached by Jiang et al [16] in a high-power plasma-assisted deposition technique.
chemical vapor deposition (PACVD). Unfortunately, the temperature reduction in this type of approach is still considered insufficient.

Considering the surface energies and thermodynamic phase stability in nanocrystalline alumina [17], another approach to synthesize and stabilize α-Al2O3 at lower temperature suggests the introduction of the isostructural nanocrystals. The surface energy during the nucleation and growth could be decreased to a relatively low level due to the additional nucleation sites or center induced by the introduced materials. Especially, the nucleation of α-Al2O3 can be facilitated by using Cr2O3 interlayers as template which is isostructural with α-Al2O3 and easily obtained at low temperature [18–21]. Diechle et al [10] reported that the deposition temperature was reduced to 500 °C by reactively sputtering Cr and Al targets and the film was detected as predominant α-(Al, Cr)2O3. Andersson et al [22] reached the same temperature by deposited α-Al2O3 films onto Cr2O3 interlayer. In addition, the α-Al2O3 seeds are also supposed to promote the low-temperature growth of the stable single-phase α-Al2O3 since the same structure to the Cr2O3 template [23, 24]. Lin et al [25] prepared Al films with α-Al2O3 seeds by glow plasma technique followed by in situ oxidation at 580 °C and the outer layer was tested as pure α-Al2O3 film. However, the pure α-Al2O3 films can still hardly be synthesized or confirmed in reactive magnetron sputtering deposition and the difference between the effects of these corundum-structured seeds have been rarely investigated.

This work aimed to identify the distinguishable effects of the corundum-structured seeds on the low-temperature growth and the mechanical property of the alumina-based films deposited by reactive RF magnetron sputtering. Two types of seeds were introduced into the films by employing the the Al + 15 wt% α-Al2O3 composite and Al100−xCrx (99.99 purity, x = 10, 20, 30) alloy as targets. Single-phase α-Al2O3 and α-type (Al0.7Cr0.3)2O3 solid solution were detected in the films deposited at 550 °C. The preferentially formed corundum-structured species could serve as seeds and induce the epitaxial growth of α-Al2O3. The phase evolution led to significant improvement of the nano-hardness and the difference of these two seeds were finally investigated.

2. Methods

The depositions of the alumina-based films were performed in a radio frequency magnetron sputtering (RFMS) system. The Al (99.99% purity) and Al100−xCrx (99.99 purity, x = 10, 20, 30) targets were commercially ordered and the Al + α-Al2O3 composite target was manufactured by powder metallurgy method using a mixture consisted of 15 wt% α-Al2O3 (99.999% purity) and 85 wt% Al (99.995% purity) powders. The dimensions of all the targets are Φ 60 mm × 3 mm and a 15 min pre-sputtering was performed to remove the contaminants on the surface in each deposition. In order to make most of the oxidation reactions of the sputtered species occur at the substrate surface, the sputtering and reaction gases were separately injected into the chamber. The inlet of the argon was in the vicinity of the sputtered target while that of oxygen was near the substrates. The Si (100) substrates (10 × 10 mm2) were cleaned in an ultrasonic device using acetone then ethanol. The distance between the target and the substrate was set as ~85 mm. The residual pressure of the vacuum chamber was evacuated to less than 5 × 10−4 Pa. The Ar gas flow was kept at 15 sccm and the O2 flow rate was 1.5 sccm. The work pressure was modified to 1.0 Pa and kept constant during the deposition. The power of the RF generator was held constant at 200 W and all the depositions were carried out at 550 °C. The deposition time for all alumina-based films was 3 h and the thickness of the films was in the range of 350 ~ 370 nm.

Electron probe microanalysis (EPMA) was performed to analyze the elemental compositions of the alumina-based films in an EPMA-1600 instrument. Grazing incident x-ray diffraction (GIXRD) was employed to characterize the phase composition of the films in a PANalytical diffractometer (Cu-Kα x-ray). Transmission electron microscopy (TEM) was carried out in a JEOL JEM-2100F system to identify the information on the microstructure of the as-deposited films. Scanning electron microscopy (SEM) was implemented in a NOVA Nanosem 430 system to observe the morphology of the alumina-based film. A thin platinum layer was sprayed on the samples to ensure that the surface conductivity is sufficient for the SEM measurement. Depth-sensing indentation (DSI) technique was performed to measure the hardness of the films in an AntonPaar NHT3 equipment. After the pre-measurement, the maximum load was set as 0.5 mN and 5 indentations were made for each sample. The Oliver and Pharr method [26] was used to calculate the values of the hardness from the obtained data.

3. Results and discussion

Table 1 shows the elemental compositions of the alumina-based films deposited from Al, Al + α-Al2O3 composite and Al100−xCrx (x = 10, 20, 30) alloy targets at 550 °C. The alumina films (sample 1 and 2) both consist of ~60 at% O and ~40 at% Al, which implies that the O/Al atomic ratio is ~1.50. The O/(Al + Cr) ratios
are also calculated and the similar value is obtained for the Al–Cr–O films (sample 3, 4 and 5) deposited from the Al–Cr alloy targets. Thus, it can be assumed that the stoichiometric alumina-based films were successfully synthesized at 550 °C with all the different targets. In addition, the calculated value of Cr/(Al + Cr) ratios are 0.31, 0.19 and 0.12 for the Al–Cr–O films deposited from Al70Cr30, Al80Cr20 and Al90Cr10 alloy targets, respectively, which suggests the great consistency between the Cr contents in Al–Cr–O films and those in alloy targets.

Figure 1 demonstrates the GIXRD patterns of alumina-based films prepared at 550 °C using Al, Al + α-Al2O3 and Al70Cr30 targets. The alumina film synthesized by using the Al target (sample 1) presents a composite phase consisted of α-Al2O3 and γ phase, which can be clarified by the dynamics of film growth. Due to the particular setting for the reaction gas inlet, most of the sputtered Al atoms or ions were oxidized immediately near the substrate surface and formed numerous alumina species. Meanwhile, the exothermal oxidation reactions emitted additional energy which could boost the surface migration of the species. Part of the species tended to stack and crystallize into α-Al2O3 while the others could only transform into metastable phases (i.e. γ or amorphous). Then, the large energy barrier suppressed the phase transition from γ to α-Al2O3 during the deposition and the metastable phases were retained in the film. Furthermore, the widen α(012) peak with low density suggests the poor crystallinity of the alumina film, which makes the assumption on the presence of amorphous phase reasonable. However, the pattern of the film prepared with the composite target (sample 2) exhibits a single phase of α-Al2O3 with high intensity peaks, while the (220) peak from γ-Al2O3 or those from other metastable phases cannot be detected. Inspired by the research reported by Lin et al [25], it can be assumed that the particles sputtered from the Al + α-Al2O3 target consist of Al atoms or ions and α-type alumina molecules. The α-type alumina molecules developing from the α-Al2O3 in the composite target would crystallize into α-Al2O3 nuclei. Meanwhile, the Al species developing from the Al in the composite were oxidized at the substrate surface and transformed into new alumina molecules accompanied with the generative heat. The heat could promote the surface migration of the alumina molecules so that these molecules could transfer to the α-type nuclei. As a result, the α-Al2O3 could grow homoepitaxially around the seeds with the formation of the metastable phases restrained.

Table 1. The elemental compositions of alumina-based films prepared with Al, Al + α-Al2O3, and Al100−xCr x (x = 10, 20, 30) targets at 550 °C.

| Sample Number | Target          | O (at%) | Al (at%) | Cr (at%) | O/Al | O/(Al + Cr) | Cr/(Al + Cr) |
|---------------|-----------------|---------|----------|----------|------|-------------|--------------|
| 1             | Al              | 60.86   | 39.14    | 1.56     |      |             |              |
| 2             | Al + α-Al2O3    | 61.74   | 38.26    | 1.61     |      |             |              |
| 3             | Al70Cr30        | 59.33   | 28.14    | 12.53    | 1.46 | 0.31        |              |
| 4             | Al80Cr20        | 60.75   | 31.72    | 7.53     | 1.55 | 0.19        |              |
| 5             | Al90Cr10        | 61.88   | 33.53    | 4.59     | 1.62 | 0.12        |              |

Figure 1. GIXRD patterns of the alumina-based films deposited at 550 °C from the Al, Al + α-Al2O3 and Al70Cr30 targets by RFMS.
The pattern of the film deposited from Al70Cr30 also exhibit the α phase only. The sputtered species containing Al and Cr atoms or ions were oxidized at the substrate surface and formed numerous Al2O3 and Cr2O3 molecules. Since the α-Cr2O3 could easily be synthesized at low temperature, the Cr2O3 molecules would preferentially condense into α-Cr2O3 nuclei. The Al2O3 molecules migrated to the α-Cr2O3 nuclei and grew heteroepitaxially as α-Al2O3. In other words, the film deposited from Al70Cr30 target is composed of α-Cr2O3 and α-Al2O3. According to the EPMA results in table 1, the content of α-Cr2O3 in this film is 30%. However, the pattern only demonstrates peaks with high density positioning around the α phases, instead of two sets of distinguishable peaks from α-Cr2O3 and α-Al2O3, respectively. Therefore, it could be assumed that these strong peaks for α phase correspond to the solid solution α-(Al0.7Cr0.3)2O3.

The films deposited from the Al80Cr20 and Al90Cr10 targets were introduced to investigate the structure evolution and confirm the formation of the α-type solid solution. Figure 2(a) presents the phase structures of the films prepared with the Al100-xCr x (x = 10, 20, 30) target at 550 °C. Compared to the film with 30% α-Cr2O3 (x = 30), the pattern of the film prepared with the Al90Cr10 target exhibits distinguishable (012) peaks from α-Cr2O3 and α-Al2O3, and the (220) peak from γ-Al2O3 can also be observed. The film deposited from Al80Cr20 demonstrates the similar phase composition composed of α-Cr2O3, α- and γ-Al2O3 with an additional weak peak of α(104). As reported in previous work [27], the Cr content in the Al–Cr–O films has a significant impact on the phase evolution. When synthesized at relatively low temperature of 550 °C, increasing the Cr content in the film could provide more α-Cr2O3 as α-type nuclei, which implies increasing the distribution density of α-Cr2O3 could promote the heteroepitaxial growth of α-Al2O3. When the α-Cr2O3 proportion reaches to 30%, the formation of γ-Al2O3 can be completely suppressed. The enlarged patterns focusing on the position of (012) peaks from α-Cr2O3 are marked as two vertical dot lines, respectively. The α-Al2O3 peaks are given in figure 2(b). The standard positions of (012) peaks from α-Cr2O3 (PDF No.38-1479) and α-Al2O3 (PDF No.10-0173) are marked as two vertical dot lines, respectively. The (012) peaks of the measured patterns locate between the reference positions. There is a trend for the α-Cr2O3 peaks to shift to higher diffraction angle as the Cr content (i.e. the α-Cr2O3 content) in the films increase. On the contrary, the α-Al2O3 peaks tend to move to the opposite direction at the same time. This phenomenon relates to the inter-substitution of the Al3+ and Cr3+ ions which results in expansion or shrink of the lattice parameters. It is well known that the Cr3+ has larger ionic radius (~0.615 Å) than Al3+ (~0.535 Å). The lattice parameters of α-Cr2O3 shrank when part of the Cr3+ were replaced by Al3+. In the same way, the lattice parameters of the α-Al2O3 expanded as some Al3+ were substituted by Cr3+. With the α-Cr2O3 content of 30% in the film deposited from the Al80Cr10 target, the (012) peaks from α-Cr2O3 and α-Al2O3 overlap into one peak, which is mostly attributed to the full inter-substitution between the metallic ions of Al3+ and Cr3+, indicating the formation of single-phase solid solution α-type (Al0.7Cr0.3)2O3 film.

To estimate the lattice size of the α-type (Al0.7Cr0.3)2O3 solid solution, the parameters can be calculated as Vegard’s law:

\[ a = x_1a_1 + x_2a_2 \]  

where \( a \) is the lattice parameter of the solid solution; \( x_1, x_2 \) and \( a_1, a_2 \) are the concentration and lattice parameter of α-Al2O3 and α-Cr2O3, respectively. For this work, the details of these two constituents are given in table 2.

Hence, the values of lattice parameters for the α-(Al0.7Cr0.3)2O3 solid solution are calculated as \( a = b = 4.8182 \) Å and \( c = 13.1720 \) Å. The interplanar spacing of (012) planes from the solid solution is also calculated as \( d = 3.5248 \) Å. So, the diffraction position of the (012) peak from the solid solution can be estimated using the
can be discovered in these TEM images. Hence, these TEM results correspond to the fast Fourier transform (FFT) patterns in the TEM image of the sample 2 and all the diffraction rings can be assigned to $\alpha$-Al$_2$O$_3$, which is consistent with the phase composition detected by GIXRD. Figure 3(b) demonstrates the selected area electron diffraction (SAED) patterns of sample 2 and all the diffraction rings can be assigned to $\alpha$-Al$_2$O$_3$, which is consistent with the phase composition detected by GIXRD (see figure 1). Figure 3(c) presents the high-resolution transmission electron microscopy (HRTEM) images of sample 2, which also confirms the distribution of the nano-crystalline $\alpha$-Al$_2$O$_3$. The enlarged view of the area marked with white box and the corresponding fast Fourier transform (FFT) patterns in figure 3(c) can be identified as the (2 12) and (2 0 4) planes of $\alpha$-Al$_2$O$_3$. Furthermore, no pattern or plane corresponding to amorphous or other metastable phases can be discovered in these TEM images. Hence, these TEM results confirm that single-phase $\alpha$-Al$_2$O$_3$ film was obtained by reactively sputtering the Al + $\alpha$-Al$_2$O$_3$ composite target at 550 °C and the formation of the metastable phases was completely suppressed.

Figure 4 shows the microstructure of the film prepared at 550 °C using the Al$_{70}$Cr$_{30}$ target (sample 3). The SAED patterns of the film in figure 4(a) exhibits $\alpha$ phase only (see figure 4(b)). According to the GIXRD patterns shown in figures 1 and 2, these diffraction rings correspond to the solid solution $\alpha$-(Al$_{0.7}$Cr$_{0.3}$)$_2$O$_3$. The enlarged view of the area marked with white box and the corresponding FFT patterns also demonstrate the planes of corundum structure. Therefore, the TEM analysis is considered consist with the GIXRD results where the single-phase solid solution $\alpha$-(Al$_{0.7}$Cr$_{0.3}$)$_2$O$_3$ film was synthesized by using Al$_{70}$Cr$_{30}$ alloy target.

The surface morphologies of the films prepared with Al, Al + $\alpha$-Al$_2$O$_3$ composite and Al$_{100-x}$Cr$_x$ (x = 10, 20, 30) alloy targets by RFMS at 550 °C are shown in figure 5. The typical granular surface is observed in each film and the uniformity of grain size may lead to the good surface quality. The grains in the film deposited from Al + $\alpha$-Al$_2$O$_3$ target are approximately twice the size of those in the film synthesized by using Al target (see figures 5(a) and (b)), which is probably attributed to the promotion of $\alpha$-Al$_2$O$_3$ nuclei on the homoepitaxial growth and crystallization. As shown in figure 5(c), the grain size of the film deposited from the Al$_{70}$Cr$_{30}$ target increases observably and is much larger than that of the alumina films. This might benefit from the oxidation of the Cr species, which could not only provide sufficient $\alpha$-type nuclei but also release the generating heat, resulting in the enhanced heteroepitaxial growth and grain growth. Moreover, there is a tendency for the grain size of the films prepared with Al–Cr alloy targets to expand as the increasing $\alpha$-Cr$_2$O$_3$ content in the films (see figures 5(d), (e) and (c)). More $\alpha$-Cr$_2$O$_3$ in the film can provide more nucleation sites or centers to promote the growth and crystallization of the $\alpha$-Al$_2$O$_3$. As shown in figure 2, these diffraction rings correspond to the solid solution $\alpha$-(Al$_{0.7}$Cr$_{0.3}$)$_2$O$_3$, which is probably attributed to the promotion of $\alpha$-Al$_2$O$_3$ nuclei on the homoepitaxial growth and grain growth. Moreover, there is a tendency for the grain size of the films prepared with Al–Cr alloy targets to expand as the increasing $\alpha$-Cr$_2$O$_3$ content in the films (see figures 5(d), (e) and (c)).

Table 2. The parameters of $\alpha$-Al$_2$O$_3$ and $\alpha$-Cr$_2$O$_3$ in $\alpha$-(Al$_{0.7}$Cr$_{0.3}$)$_2$O$_3$ solid solution.

| Constituents | Concentration | Reference (PDF No.) | $a$ (Å) | $b$ (Å) | $c$ (Å) |
|--------------|---------------|---------------------|--------|--------|--------|
| $\alpha$-Al$_2$O$_3$ | 70%          | 10-0173             | 4.7580 | 4.7580 | 12.9910 |
| $\alpha$-Cr$_2$O$_3$ | 30%          | 38-1479             | 4.9588 | 4.9588 | 13.5942 |

Figure 3. TEM micrograph of the film deposited from Al + $\alpha$-Al$_2$O$_3$ target at 550 °C: (a) TEM image; (b) the SAED pattern and (c) the HRTEM image.
nucleation during the deposition progress, which implies that the required energy for nucleation was reduced and more energy could be expended for grain growth. However, the distinguishable grain size of the films is in the range of a dozen to dozens of nanometers, which illustrates the formation of the nanocrystal alumina-based films. The cross-section view of these alumina-based films are similar to each other and the thickness are measured as 350 \(\sim\) 370 nm (not shown here). Based on the deposition time of 3 h, the deposition rate of these films is in the range of 117 \(\sim\) 123 nm/h, which could be considered at a relatively low level. However, this low deposition rate may also have a positive effect on the formation of corundum-structured phase at low temperature since the species have sufficient time for surface migration. On the contrary, the kinetics of nucleation and growth of the \(\alpha\) phase at larger rate may be unfavorable and higher deposition temperature will be required.

The nano-hardness of the alumina-based films were evaluated by the nano-indentation measurement. The load versus displacement (P-h) curves of the films prepared with Al, Al + \(\alpha\)-Al\(_2\)O\(_3\), Al\(_{70}\)Cr\(_{30}\), Al\(_{90}\)Cr\(_{10}\) and Al\(_{80}\)Cr\(_{20}\) targets are show in figure 6(a) and those curves of the films despoted from the Al–Cr alloy targets are demonstrated in figure 6(b). The value of the calculated hardness \((H)\) are given in figure 6(c). The hardness of the alumina-based films are mostly ascribed to the type and amount of the phases in the films. As a reference, the hardness of the amorphous, \(\gamma\)- and \(\alpha\)-Al\(_2\)O\(_3\) films deposited by magnetron sputtering has been reported as \(\sim 10\) GPa, \(\sim 19\) GPa and \(\sim 22\) GPa, respectively [12]. According to the phase composition analysis (see figure 1),

Figure 4. TEM micrograph of the film deposited from Al\(_{70}\)Cr\(_{30}\) target at 550 °C: (a) TEM image; (b) the SAED pattern and (c) the HRTEM image.

Figure 5. Top-view of SEM images of the films deposited at 550 °C by RFMS from (a) Al, (b) Al + \(\alpha\)-Al\(_2\)O\(_3\), (c) Al\(_{70}\)Cr\(_{30}\), (d) Al\(_{90}\)Cr\(_{10}\) and (e) Al\(_{80}\)Cr\(_{20}\) targets.
the presence of γ and amorphous phases lead to a relatively low hardness of ∼16.3 GPa for the film prepared with Al target. On the other hand, the film synthesized by sputtering the Al + α-Al2O3 composite target exhibits single-phase α-Al2O3 only, which increases the hardness to ∼23.5 GPa, corresponding to the hardness of the bulk α-Al2O3 materials. However, the α-(Al0.7Cr0.3)2O3 film deposited from Al70Cr30 target presents highest hardness of ∼28.5 GPa despite the similar hardness between the α-Al2O3 and α-Cr2O3, which is mostly ascribed to the solution strengthening.

According to the GIXRD results shown in figure 2, it can be assumed that the film prepared with Al90Cr10 alloy shows relatively low hardness of ∼16.7 GPa due to the existence of γ-Al2O3 and amorphous phase. The low α-Cr2O3 content (10%) in the film can barely provide sufficient α-type nuclei and the heteroepitaxial growth of the α-Al2O3 has been greatly limited, which results in a similar growth pattern to the film deposited from Al target. When the Cr2O3 content increases to 20%, the hardness of the film increases to 20.2 GPa with the enhanced growth of the α-Al2O3. However, the formation of γ-Al2O3 or amorphous phase can hardly be completely suppressed and the value of the hardness is still slightly lower than that of the film composed of single-phase α-Al2O3. Owing to the combined contribution of the single α phase and the solution strengthening, the hardness of the film deposited from Al70Cr30 target reaches a highest value of 28.5 GPa. In a word, the α-Al2O3 seeds in the film could suppress the formation of metastable phases and lead to the pure α-Al2O3 films with high hardness. The α-Cr2O3 seeds with certain distribution density could not only play the same role in the synthesis of single-phase α-type films but also induce the solution strengthening for the full inter-substitution between the metal ions.

4. Conclusions

Two types of corundum-structured seeds were introduced into alumina-based films by using Al + α-Al2O3 (15 wt%) composite and Al100−xCrx (x = 10, 20, 30) alloy as targets via radio frequency magnetron sputtering. The epitaxial growth of the α-Al2O3 is enhanced by the presence of these seeds and the nucleation of γ or other metastable phases is suppressed in the meantime. The nanocrystalline single-phase α-Al2O3 film was synthesized by using the Al + α-Al2O3 composite target at 550 °C. The homoepitaxial growth of α-Al2O3 at low temperature was promoted by the existence of α-Al2O3 nuclei, which leads to a hardness of ∼23.5 GPa. The

Figure 6. P-h curves of the alumina-based films deposited at 550 °C from (a) the Al, Al + α-Al2O3; and Al70Cr30 targets and (b) the Al100−xCrx (x = 10, 20, 30) alloy targets and (c) the calculated hardness of the films.
single α-type (Al0.7Cr0.3)xO2 solid solution film with hardness of ~28.5 GPa was synthesized at 550 °C using Al70Cr30 alloy as target. The high hardness of the α-(Al0.7Cr0.3)xO2 film is ascribed to the combined effects of sufficient distribution density of corundum-structure nuclei (i.e. α-Cr2O3) and solution strengthening.

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References

[1] Bourzakis K-D, Michailidis N, Skordaris G, Bouzakis E, Biermann D and M’Saoubi R 2012 Cutting with coated tools: coating technologies, characterization methods and performance optimization CIRP Ann. Manuf. Technol. 61 703–23
[2] Bobzin K, Bagcivan N and Ewerling M 2010 Crystalline gamma-alumina deposited in an industrial coating unit for demanding turning operations Adv. Eng. Mater. 12 1275–9
[3] Bobzin K, Hirt G, Bagcivan N, Khizhnyakova L and Ewerling M 2011 Crystalline gamma-Al2O3 physical vapour deposition-coating for steel thixoforming tools J. Nanosci. Nanotechnol. 11 8782–5
[4] Edlmayr V, Moser M, Walter C and Mitterer C 2010 Thermal stability of sputtered Al2O3 coatings Surf. Coat. Technol. 204 1576–81
[5] Eklund P, Sridharan M, Singh G and Böttiger J 2009 Thermal stability and phase transformations of gamma- -amorphous-Al2O3 thin films Plasma Process. Polym. 6 S907–11
[6] Musil J, Blazek J, Zeman P, Prokova S, Sasek M and Cerstvy R 2010 Thermal stability of alumina thin films containing gamma-Al2O3 phase prepared by reactive magnetron sputtering Appl. Surf. Sci. 257 1058–62
[7] Edlmayr V, Harzer T P, Hoffmann R, Kiener D, Scheu C and Mitterer C 2011 Effects of thermal annealing on the microstructure of sputtered Al2O3 coatings J. Vac. Sci. Technol. A 29 041506–8
[8] Bobzin K, Bagcivan N, Reinholdt A and Ewerling M 2010 Thermal stability of gamma-Al2O3 coatings for challenging cutting operations Surf. Coat. Technol. 205 1444–8
[9] Ruppi S 2005 Deposition, microstructure and properties of texture-controlled CVD α-Al2O3 coatings, Int J. Refract. Met. Hard Mater. 23 306–16
[10] Diechle D, Stueber M, Leiste H, Ulrich S and Schier Y 2010 Combinatorial approach to the growth of α-(Al1−xCr)xO3 solid solution strengthened thin film by reactive r.f. magnetron sputtering Surf. Coat. Technol. 204 3258–64
[11] Zyweitzki O, Hoetzsch G, Fietzke F and Goedicke K 1996 Effect of the substrate temperature on the structure and properties of Al2O3 layers reactively deposited by pulsed magnetron sputtering Surf. Coat. Technol. 82 169–75
[12] Zyweitzki O and Hoetzsch G 1996 Influence of coating parameters on the structure and properties of Al2O3 layers reactively deposited by means of pulsed magnetron sputtering Surf. Coat. Technol. 86–87 640–7
[13] Wallin E, Selinder T J, Elfwing M and Helmersson U 2008 Synthesis of α-Al2O3 thin film using reactive high-power impulse magnetron sputtering Europhys. Lett. 82 36002
[14] Selinder T J, Coronel E, Wallin E and Helmersson U 2009 α-Alumina coatings on WC/Co Substrates by physical vapor deposition Int. J. Refract. Met. Hard Mater. 27 507–12
[15] Brill R, Koch F, Mazurek J, Levcuk D, Balden M, Yamada-Takamura Y, Maier H and Bohl H 2003 Crystal structure characterization of filtered arc deposited alumina coatings temperature and bias voltage Surf. Coat. Technol. 174–175 606–10
[16] Jiang K Y, Saraknos K, Konstantinidis S and Schneider JM 2010 Low temperature synthesis of α-Al2O3 films by high-power plasma-assisted chemical vapor deposition J. Phys. D: Appl. Phys. 43 32502
[17] McHale M J, Auroux A, Perrotta A J and Navrotsky A 1997 Surface energies and Thermo- dynamic phase stability in nanocrystalline aluminas Science 277 788–91
[18] Jin F, Xu G, Tazawa M, Yoshimura K, Musica D, Alami J and Helmersson U 2002 Low temperature deposition of α-Al2O3 thin films by sputtering using a Cr2O3 target J. Vac. Sci. Technol. A 20 2134–6
[19] Wallin E, Andersson J M, LattelMann M and Helmersson U 2008 Influence of residual water on magnetron sputtered crystalline Al2O3 thin films Thin Solid Films 516 3877–83
[20] Kohara T, Tamagaki H, Ikari Y and Fuji H 2004 Deposition of α-Al2O3 hard coatings by reactive magnetron sputtering Surf. Coat. Technol. 185 166–71
[21] Cai J, Xu B and Ling G 2013 Observation on the interface of α-Al2O3/Cr2O3: prepared by oxidation of Al2O3/Cr Appl. Surf. Sci. 268 111–6
[22] Andersson J M, Wallin E, Helmersson U, Kreissig U and Münger P E 2006 Phase control of Al2O3 thin films grown at low temperature Thin Solid Films 513 57–62
[23] Xie Z P, Lu J W, Huang Y and Cheng Y B 2003 Influence of α-alumina seed on the morphology of grain growth in alumina ceramics from Bayer aluminum hydroxide Mater. Lett. 57 2501–8
[24] Sahar F S and Fang T T 1999 Low-temperature synthesis of α-alumina using citrate process with α-alumina seeding Mater. Chem. Phys. 60 91–4
[25] Lin Y B, Wang C and Tao J 2013 Induction effect of α-Al2O3 seeds on formation of alumina coatings prepared by glow plasma technique Surf. Coat. Technol. 235 544–51
[26] Oliver WC and Pharr GM 1992 An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation J. Mater. Res. 7 1564–83

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[27] Cheng Y T, Qiu W Q, Zhou K S, Jiao D L, Liu Z W, Zhong X C and Zhang H 2019 The influence of Cr content on the phase structure of the Al-rich Al–Cr–O films deposited by magnetron sputtering at low temperature Ceram. Int. 45 8175–80