Investigation on the structural and mechanical properties of anti-sticking sputtered tungsten chromium nitride films

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A B S T R A C T
Tungsten chromium nitride (WCrN) thin films are prepared by dual-gun co-sputter process. As the surface coatings on the molding die for glass forming, WCrN films show less deterioration at high temperature than the conventional CrN coating. WCrN thin films are deposited via the reactive co-sputtering of Cr/W targets. The working pressure is kept at 2.66 Pa and the argon/nitrogen ratio is 10. Applied power of chromium is fixed and the applied power of tungsten is varied. Experimental results indicate that the atomic ratio of tungsten in the films increases with the applied power of tungsten. The dominant crystalline phase is chromium nitride when the tungsten target power is below 100 W, while tungsten nitride dominates in the film structure when the tungsten target power is beyond 200 W. A dense structure with much finer particles is developed as the tungsten power is 200 W. As the power is increased to 300 W, the particles become coarser in size. The film roughness exhibits a decreasing trend at low tungsten power and then increases as the tungsten power increased up to 300 and 400 W, presumably due to the phase change from chromium nitrides to tungsten nitrides. Further annealing of the WCrN thin films is simulated as the glass molding condition to check the anti-sticking property which is a critical requirement in molding die surface coating application. The WCrN thin film coating shows good anti-sticking property at 400 °C annealing when the tungsten target power is 200 W.

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1. Introduction

Glass molding technology is attracting attention because small scale optical lenses are widely used in electronic products. Heating, molding and annealing are the three stages of the glass molding process [1]. Concerning the design of the molding die for highly accurate aspherical glass molding, critical issues include surface roughness, hardness, and adhesion. Extending the lifetime of the molding die can be beneficial to the cost reduction. The protective films deposited onto the molding dies can prolong the application lifetime of the die materials. Noble metals, such as Pt, Ir and Ru are deposited on tungsten carbide molds. However, alternative surface coatings are investigated due to cost consideration. Chromium nitride (CrN) is a promising candidate for improving the useful lifetime of steel tools and related components [2–8]. CrN films containing tungsten additive have been studied and are found to have excellent hardness, adhesion, anti-oxidation and wear resistance properties [2,9,10].

In this work, tungsten chromium nitride (WCrN) thin films are deposited using a dual gun sputtering technology [9]. The applied power of chromium target is fixed and the effects of applied power for tungsten target are investigated. The roughness, hardness and the phase evolution of the WCrN films are extensively investigated as well as the anti-sticking behavior as glass molding die surface coating.

2. Experimental procedures

WCrN films are deposited on Si substrate and WC substrates using a dual gun sputtering apparatus with pure chromium and tungsten metal targets. Table 1 presents the experimental deposition parameters. The thickness of the coating is around 1.2 μm.

X-ray diffraction with monochromatic Cu Kα source (XRD, PANalytical XPert PRO MRD) is used to investigate the crystallinity of the films by grazing incident configuration and the angle between X-ray incident beam and film surface is set at 2°. Diffraction peaks of the crystalline phase are compared with those of standard compounds in the JCPDS data file. A scanning electron microscope (SEM, JEOL JSM-7000F) is used to observe the surface morphology and cross-section images with an accelerating voltage of 15 kV. The elemental distribution of the thin films is examined by wavelength dispersive
X-ray spectrometer (WDS). The surface roughness is examined using a multi-mode atomic force microscope (AFM, VEECO Dimension 3100). The film average surface roughness (Ra) can be obtained by measuring the deflection produced by a sharp tip on micron-sized cantilever on AFM contact mode. The film micro-hardness values are calculated from the results of a nano-indentation test (TriboLab, Hysitron, USA).

Fig. 1 presents the schematic illustration of glass molding situation with WCrN coatings on the molding die and the glass material (K-PG325). For the glass material, the transition and yielding point temperatures are 288 °C and 317 °C, respectively. The testing die with WCrN surface coating is then annealed at 400, 500 °C to simulate the glass molding situation in an atmosphere of air for 15 min.

3. Results and discussion

Fig. 2 shows the XRD pattern of the WCrN films. The standard diffraction patterns of possible phases, including CrN, WN, and W are provided for comparison. The full width at half maximum of the diffraction peaks of W (110) decreases as the tungsten power increases. The peak of CrN (200) disappears when applied at 200 W. The W (220) and W (211) peaks were obvious at 400 W. The dominant crystalline phase is chromium nitride when the tungsten target power is below 100 W, while pure tungsten and tungsten nitride dominate in the film structure when the tungsten target power is beyond 200 W. At tungsten target power of 200 W, CrN, WN, and W seem to co-exist in the film structure, and this may account for the good surface flatness as discussed in the microstructure and roughness results as well as the good anti-sticking property. Fig. 3 shows the quantitative (WDS) analysis of the as-deposited WCrN films as a function of the tungsten target power. The results indicate that the atomic ratio of tungsten increases with tungsten power accordingly. The sputtering energy is proportional to the tungsten power since the other process parameters are fixed, resulting in the increase of tungsten content in the films.

Fig. 4 shows the SEM microstructure of the WCrN film surface as a function of the tungsten target power. A denser structure with much finer particle can be observed as the tungsten target power is increased from zero to 200 W. As the tungsten target power increases beyond 300 W, coarser particles are formed. From AFM results, Fig. 5 shows the particle size as a function of tungsten target power. Fig. 5 also shows the surface roughness in the WCrN films. For the as-deposited WCrN films, the roughness decreases as the tungsten target power increases from zero to 200 W, and this agrees well with the SEM images. With increasing tungsten target power beyond 300 W, the film roughness increases. Wuhrer et al. [11] investigated the effect of the depositing energy on the nano-structured coating and concluded that the deposited atoms/molecules have a high capacity to be rearranged; the surfaces of their coatings became smoother as the depositing energy increased with tungsten power. However, a rougher surface is observed when the tungsten target power increases to 300 W. It is presumably because increasing the tungsten target power enhances the probability of collision between chromium and nitrogen. This will reduce the mobility and diffusion of atoms at the surface of the specimen and form a rougher surface as well. Fig. 6 shows the hardness of the WCrN films deposited at different tungsten target powers. The hardness increases with tungsten target power.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
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<tr>
<td>Target</td>
<td>Cr/W</td>
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<tr>
<td>Reactive gas</td>
<td>Ar/N2</td>
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<td>Working pressure (Pa)</td>
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<td>Tungsten pulse power (W)</td>
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<td>Substrate bias (−V)</td>
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<tr>
<td>Argon:nitrogen flow</td>
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</table>

Fig. 1. Schemes of the coating/glass system under the glass molding process.

Fig. 2. XRD patterns of the as-deposited WCrN films prepared at various tungsten powers.

Fig. 3. The WDS analysis of the as-deposited WCrN films at various tungsten powers.
From the WDS analysis, increasing the tungsten power increases the tungsten content in the film. From the literature, tungsten-containing films have more covalent bonding than CrN [10] and the more covalent bonding character of the WCrN films prepared at high tungsten target power accounts for the difference in hardness [2].

Fig. 7 (a) and (b) illustrates the crystalline evolution after annealing at 400/500 °C, respectively. A non-sticking material must resist oxidation. The oxide phase identified as Cr₂O₃ appears in Fig. 7 (b) when the film annealed at 500 °C and this phase does not favor optical precision. Suitable annealing temperature at 400 °C is close to the actual glass molding application temperature and no oxide phase can be found under this temperature. Heat treatment releases the compressive stress causing the CrN and WN peaks to be shifted to a higher angle than in Fig. 2. The peak shift reduces the lattice spacing according to Bragg’s law. Fig. 8 shows the lattice spacing of CrN (111) as a function of the tungsten power. The lattice spacing following heat treatment at 500 °C is lower than that of the as-deposited films. Fig. 9 shows the surface roughness values of the as-deposited and annealed assemblies of the specimens. The maximum roughness of the WCrN films is found to be less than 8 nm, which is acceptable in the application as glass molding die [9]. Annealing at 500 °C in air reduces the surface roughness of the WCrN films. The limitation on grain growth may have been responsible for the decrease in roughness [8].

The most critical requirement for a glass molding die is that the die-surface has to be non-sticking with glass in the application situation at high temperature. Such glass sticking at elevated temperature may result in poor adhesive wear property and cause damage to the glass product as well as the die surface. It occurs if the contact temperature is high enough to decrease the viscosity of the liquid glass at the contact interface and to overcome the surface tension of the molten glass. Fig. 10 shows the topography images of the glass residues on the WCrN films after annealing at 400 and 500 °C.
anti-sticking behavior for the WCrN films annealed at 400 °C is good since no glass residue can be found on the glass molding die surface. On the other hand, glass residues are clearly observed for the WCrN films annealed at 500 °C. Localized area with a limited volume of glass residue or severe glass sticking combined with film delamination can be observed. Based on the crystallography, microstructure, surface roughness and anti-sticking property investigation, WCrN films prepared with tungsten target power of 200 W and annealed at 400 °C are proved to be the best glass molding die surface coating in the application.

4. Conclusions

WCrN films are deposited on silicon wafer and WC substrates using a dual gun sputtering system with pure chromium and tungsten metal targets. This study investigates the effect of tungsten target power. The WDS analysis of the WCrN films indicates that the atomic ratio of tungsten increases with tungsten power. The roughness and particle size decrease as the tungsten power is increased from zero to 200 W and then increase with a further increase in the tungsten power. The more covalent bonding character of the WCrN films accounts for the difference in film hardness. The anti-sticking behavior of the WCrN films annealed at 400 °C is observed, whereas the WCrN films annealed at 500 °C exhibit poor anti-sticking behavior due to the occurrence of chromium oxide at this temperature. Based on the crystallography, microstructure, surface roughness and anti-sticking property investigation, WCrN films prepared with tungsten target power of 200 W and 400 °C annealing exhibit the best glass molding die surface coating in the application.

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References

Fig. 10. SEM micrographs of WC\textsubscript{N} films after heat treatment at (a) 400 °C and (b) 500 °C simulating a glass molding process.