Processing of ultra-hard coatings based on AlMgB₁₄ films

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Abstract First time AlMgB₁₄ films were prepared in Ames Lab by pulsed laser deposition technique. In this work, RF magnetron sputtering from a single stoichiometric target was employed to fabricate hard AlMgB₁₄ coatings on Si wafer and industrial items. Measurements of nanohardness and elastic Young’s modulus were performed to determine reliable strength characteristics of samples. Smooth 3 μm thick AlMgB₁₄ films with the RMS surface roughness to be less than 1 nm exhibit hardness of 34 GPa and modulus of elasticity of 230 GPa at 20 mN peak load.

1. Introduction
Development and application of wear-resistant coatings is one of the main directions in the field of protection against wear and tear of the surface layer of cutting tools and saving their geometry at processing. Coatings based on aluminum magnesium boride AlMgB₁₄ (BAM films) demonstrate at small contact depths nanohardness up to 51 GPa [1] and have great potential for industrial applications.

For today, the coating was fabricated by pulsed laser deposition (PLD) technique [1, 2], but in terms of industrial application the most promising method is a magnetron sputtering technique. It enables preparation of conformal film coatings onto complex shaped and big size substrates. Several attempts to fabricate the coatings by RF magnetron sputtering were undertaken [3–6]. However, we know only one successful result published to date [7]. This work aims to further develop sputtering technology for ultra-hard AlMgB₁₄ coatings fabrication.

2. Materials and methods
BAM films are RF magnetron sputtered from a single 2 inch stoichiometric ceramic AlMgB₁₄ target in AJA Orion 5 system. Target was fabricated from elemental aluminum (99.97% pure), magnesium (99.8% pure) and boron (99% pure). The simultaneous synthesis and consolidation of AlMgB₁₄ from powder mixtures was performed in a spark plasma sintering apparatus [8].

To obtain films with the required stoichiometric composition and specific properties the parameters of sputtering are modified: target sputtering power (50 – 200 W), substrate temperature (200 – 450°C), target-to-substrate distance (10 – 35 mm), the pressure in vacuum chamber (2 – 5 mTorr of Ar gas), and time of sputtering (30 – 60 min).

Atomic-force microscope (AFM) CMM-2000 and scanning electron microscope (SEM) HITACHI SU1510 are used to control, respectively, films’ roughness and stoichiometry by energy dispersive X-ray spectroscopy (EDX). Mechanical tests are carried out using desktop nanohardness tester NHT2- TTX with Berkovich three-sided diamond pyramid tip. Peak load was varied from 1 to 20 mN, loading
and unloading time was 30 s, dwelling time was zero. Hardness $H$ and Young’s modulus $E$ are obtained as per the Oliver and Pharr method. Effective elastic modulus $E_{\text{eff}}$ is instrumentally measured through the indents contact area and unloading stiffness. Young’s modulus we calculate $E = E_{\text{eff}} (1-\nu^2)$ assuming BAM film Poisson’s ratio $\nu$ to be equal to 0.25.

Crystal structure of deposited films is determined by X-ray diffraction (XRD) using Cu$K_{\alpha}$ radiation.

3. Results and discussion

Result of X-ray examination is presented in figure 1. X-ray spectrum shows that BAM film is amorphous, diffraction peaks belong to Si(100) wafer used as a substrate.

![X-ray diffraction spectrum of BAM film deposited on Si(100) wafer.](image)

Films deposited during 40 min without substrate heating at the distance of 35 mm from the target, at 200 W of RF power, and 5 mTorr of Ar gas pressure had low hardness and substantial degree of roughness.

The next series of samples was obtained at target-to-substrate distance equal to 10 – 12 mm and target sputtering power 200 – 250 W. Figure 2 and table 1 present characteristics of EDX spectrum and optical micrograph of island-like surface of sample «RF6» fabricated at these conditions. Sputtered film appeared to be inhomogeneous and besides Al, Mg and B contains also C, N, and O.

![Optical micrograph of the surface of film «RF6» deposited at target sputtering power equal to 250 W and target-to-substrate distance of 12 mm.](image)

![EDX spectrum of sample «RF6» recorded at acceleration voltage of 10 kV.](image)
Table 1. Ratio of the elements in the sample «RF6».

| Element | Weight % | Weight % Error | Atom % | Atom % Error |
|---------|----------|----------------|--------|--------------|
| B - K   | 46.05    | ± 0.79         | 61.53  | ± 1.07       |
| C - K   | 4.70     | ± 0.74         | 5.66   | ± 0.89       |
| N - K   | 2.12     | ± 0.92         | 2.19   | ± 0.95       |
| O - K   | 13.72    | ± 0.49         | 12.39  | ± 0.44       |
| Mg - K  | 6.76     | ± 0.23         | 4.02   | ± 0.14       |
| Al - K  | 24.79    | ± 0.36         | 13.27  | ± 0.19       |
| Si - K  | 1.86     | ± 0.12         | 0.95   | ± 0.06       |
| Total   | 100.00   |                | 100.00 |              |

Table 2 presents results of nanoindentation test for samples «RF4» and «RF6». Hardness of sample «RF4» at 20 mN peak load in the flat surface outside the «islands» area is 33.7 GPa and Young’s modulus is 182 GPa. For the sample «RF6», hardness and Young’s modulus slightly vary within the error ranges as, respectively, 39 – 37 GPa and 245 – 270 GPa.

Table 2. Nanoindentation data recorded at 20 mN peak load for samples «RF4» and «RF6» deposited at target-to-substrate distances 35 and 12 mm, correspondingly.

| Characteristics | Sample «RF4» | Sample «RF6» within «islands» | Sample «RF6» outside «islands» |
|-----------------|--------------|-------------------------------|--------------------------------|
| Penetration depth $h_{max}$, μm | 0.26         | 0.24                          | 0.23                          |
| Hardness $H$, GPa   | 33.7 ± 1.6   | 37 ± 6                        | 39 ± 7                        |
| Young’s modulus $E$, GPa | 182 ± 3      | 270 ± 40                      | 245 ± 16                      |
| Elastic strain index $H/E$ | 0.19         | 0.14                          | 0.16                          |

To achieve smooth films’ surface we modified processing conditions. Reducing power to 100 – 150 W (target sputtering power density of 5 – 7.5 W/cm²) sputtered films appeared to be largely smooth. Surface morphology of deposited samples was investigated using AFM at square areas from 1 × 1 μm² (figure 3) to 8 × 8 μm². Root-mean-square (RMS) surface roughness of 2.6 μm thick film was found to be less than 1 nm.

Figure 3. 3D AFM image of sample surface with the size of 1 × 1 μm².

The following two stage sputtering procedure enabled accomplishment of ultimate characteristics of AlMgB₁₄ films:
- smooth thin template layer was deposited at low target sputtering power of 50 W during 10 – 15 min;
- sputtering of top layer lasted 40 – 50 min at high target sputtering power 100 – 200 W.
Both layers were deposited at the same target-to-substrate distance of 20 mm. Between two processing stages, target sputtering power was changed slowly (1 W/s) increasing to a predetermined level. Films thus obtained had no unevenness. It is worth noting that although a substrate was not specially heated, at short distances it was warmed up by plasma discharge. With a thermocouple, we determined temperature of 7 cm$^2$ square area of substrate to be 200, 350, and 450$^\circ$C at, respectively, 100, 150, and 200 W of sputtering RF power.

Figure 4 and table 3 present example of 20 mN load-penetration depth chart and results of nanoindentation tests for «RF8» sample deposited in two stages process at RF power equal to 150 W.

![Figure 4. Typical load-penetration depth chart recorded for «RF8» sample at applied peak load $F_{\text{max}} = 20$ mN.](image)

Data in table 3 are portrayed also in figure 5. They clearly reflect the presence of strong indentation size effect (ISE) found earlier in [1, 7]. Both hardness and Young’s modulus sharply increase at shallow penetration depths when loads diminish. Hardness and Young’s modulus attain the peak values of, respectively, 61 and 488 GPa at 1 mN and reach the saturation of 34.3 and 229 GPa at 20 mN.

![Figure 5. Hardness (a) and Young’s modulus (b) in sample «RF8» at various loads ranged 1 to 20 mN.](image)

$H$ and $E$ data for all the indentations made at different loading forces are collected in figure 6. They
group themselves along the straight line \( H = 0.14 \) \( E \). The ratio of nanohardness \( H \) to Young’s modulus \( E \) is known as the elastic strain index and considered as an indicative measure of the wear resistance of materials. It is commonly assumed that a material with high \( H/E \) ratio like 0.1 possesses a better wear resistance than a material with a low ratio \( H/E \sim 0.01 \). In figure 6 we compared this characteristic of «RF8» film with those in several engineering materials.

![Figure 6](image)

**Figure 6.** Elastic strain index as high as 0.14 in magnetron sputtered AlMgB\(_{14}\)/Si(100) film «RF8» compared with \( H/E \) ratio in various known materials.

Also, we attempted to coat a surface of some commercial industrial items. Magnetic steel 5 mm in diameter hemispheric ball on the small leg used as a head of special gauge was chosen as an example. Accurate cleaning and polishing of specimen’s surface preceded BAM coating. At first, organic contaminants were removed with the ethanol. Then, mechanical polishing of ball’s surface was made in two steps:

1. polishing using paste Pikal\(^\circ\) (5 – 10 min);
2. polishing with clean dry felted fabric (5 – 10 min).

Quantitative AFM analysis of polished surface resulted RMS roughness equal to 20 – 100 nm within required operational area.

Smooth AlMgB\(_{14}\) film was deposited to the ball item’s surface according to the procedure similar to sample «RF8». The first template layer was deposited at the distance of 18 mm and RF power of 70 W. Subsequently, target sputtering power was increased up to 150 W.

Figure 7a shows ball’s surface is almost completely smooth except few dust particle contaminants. Figure 7b confirms that whole ball item’s coated surface consists of light elements (B, Al and Mg). Hardness and Young’s modulus obtained at 40 mN peak load were found to be 35 – 38 GPa and 250 - 350 GPa, correspondingly.
4. Conclusion
Hardness of magnetron sputtered AlMgB$_{14}$ films can be enhanced at reduced target-to-substrate distance and increased target sputtering power. Unfortunately, both above mentioned conditions lead to a roughening of coated surfaces. Nevertheless, a wide range of processing parameters exists to find smooth surface – high hardness tradeoff and to achieve ultimate properties of magnetron sputtered BAM coatings required for any special application.

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