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Bias effects on AlMgB thin films prepared by magnetron sputtering

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AlMgB thin films were deposited on silicon (100) substrate using a three-target magnetron sputtering system in argon atmosphere. The influence of negative bias voltage on the thickness, morphology, microstructure, local bonding and hardness of the deposited films was investigated. Experimental results show that all films are X-ray amorphous, and the properties of the deposited films have a strong dependence on the applied substrate's negative bias voltage. Deposited at high negative bias voltage, the AlMgB thin films are found to be generally dense, having a smooth surface and containing more well-formed B_{12} icosahedra, which consequently increase the hardness of the deposited films. However, deposited at low negative bias voltage, the AlMgB thin films exhibit loose structure, coarse surface and contain few B_{12} icosahedra. It is shown that the hardness of the dense and smooth AlMgB thin films can reach 22 GPa at the negative bias voltage of 400 V.

Keywords: AlMgB thin films, Magnetron sputtering, Negative bias voltage, Thickness, Hardness

Introduction

Since the discovery of superconductive MgB_2,[1] considerable attention has been paid to boron and boron-rich compounds. One of these compounds that deserves to be mentioned is the intermetallic orthorhombic $AlMgB_{14}$, which was firstly reported by Matkovich and Economy[2] and then refined by Higashi and Ito.[3] The outstanding structure of $AlMgB_{14}$ is a body-centred orthorhombic arrangement, in which there are four B_{12} icosahedra containing 64 atoms [space groups Imam (74), $a = 0.5848$ nm, $b = 0.8112$ nm, $c = 0.0312$ nm]. Different from conventional materials (e.g., diamond and cubic-BN), this special crystal texture contributes to excellent properties, such as high hardness,[4] low density[5] and high thermal stability.[6] Owing to these remarkable properties, $AlMgB_{14}$ has been seen as a promising candidate material in cutting tools, protective coating and microelectromechanical components.[7]

Up to now, $AlMgB_{14}$ has been prepared by several methods in bulk or power form.[8,9] Moreover, several works have reported the preparation of AlMgB thin films by magnetron sputtering.[10] Actually, many methods can be used to deposit hard coatings, such as chemical vapour deposition[11] and physical vapour deposition (PVD).[12] Among these methods, PVD outstands because the compound films can be deposited at relatively lower substrate temperatures. As one of the typical PVD methods, magnetron sputtering is widely used in the hard coatings, which has lots of remarkable merits, such as increasing the density of deposited film, forming film with smooth surface and being suitable for large-scale production.[13]

In magnetron sputtering, the influence of deposition parameters on structure and properties of AlMgB thin films has been extensively studied in recent years. Yan *et al.*[14] explored the effects of AlMg alloy target on the hard films of AlMgB ternary matrices. Wu *et al.*[15] investigated the relationship between deposition temperature and target power. Kang *et al.*[16] discussed the effects of deposition pressure. However, the effects of the negative substrate bias voltage on the structure and properties of the AlMgB thin films are scarcely reported in the series. Actually, ion bombardment in the vicinity of substrate can be significantly enhanced by applying the negative bias voltage, leading to higher adatom mobility, more desorption and displacement of surface atoms.[17] Thus the structure and properties of AlMgB (e.g., the surface and mechanical properties) can be improved by varying the negative bias voltage. The important influence of bias voltage on other coatings, such as CrTiAlN and AlCrTiWNbTa, has been demonstrated.[17,18] Therefore, there is a great need for understanding of the relationship between negative bias voltage and AlMgB thin films. It is of great value to cover the absence and lay the foundation for practical applications of AlMgB thin films.

In the present work, we prepared AlMgB thin films using magnetron sputtering, and explored the influence of negative bias voltage on the thickness, morphology, microstructure, local bonding and mechanical of AlMgB thin films in detail.

Experimental methods

AlMgB thin films were deposited on Si (100) substrates by a three-target magnetron co-sputtering system in an argon

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(Ar) atmosphere. A sintered boron disk (purity: 99.9%), an aluminium (purity: 99.99%) disk and a magnesium (purity: 99.99%) disk with the diameter of 75 mm were used as targets. A substrate holder was located 110 mm away from the targets. To construct homogeneous thin films and avoid layer structure, the substrates were located at the rotating rack with 6 rev min^{-1}. All substrates were cleaned following a conventional cleaning process. The substrates were ultrasonically cleaned in acetone, ethanol and deionised water in sequence, and then blow-dried with nitrogen gas. Following this wet cleaning procedure, the substrates were then in situ cleaned by reverse sputter etching in argon discharge with the negative bias voltage of 650 V for 15 minutes. Prior to the actual film deposition, all samples were pre-sputtered for 10 minutes to remove any residual contaminants or surface oxides. The detail parameters are shown in Table 1.

A 3D surface profiler (ZYGO, New View 5022) was performed to obtain the film thickness by partly masking the substrate surface and measuring the height of the step. The cross-sectional morphology structures of the films were investigated by scanning electron microscope (SEM, Supra 55 Sapphire). Atomic force microscope (AFM, CSPM5000) was applied to obtain the root mean square roughness (RMS) over the scan area of $4 \times 4\ \mu m^2$ in a tapping mode. The crystal structure of films was investigated by X-ray diffraction (XRD, Bruker Discover 8) using Cu K_α radiation ($\lambda = 0.15418$ nm) with an incident angle of 2°. The local bonding information was extracted by Fourier transforms infrared spectroscopy (FTIR, NEXUS). Nanoindentation experiments were carried out using the MTS XP system with a Berkovich diamond indenter to test the hardness and elastic modulus. And the maximum contact depth was less than 14% of the obtained film thickness (600–1400 nm) to ensure that the intrinsic properties of the films were not affected by the soft silicon substrates. Each sample was measured for nine times and the values of hardness and Young's modulus were determined from the mean value of these several measurements.

Results and discussion

Thickness analysis

Figure 1 shows the thickness of AlMgB thin films as a function of the negative bias voltage. As can be seen, the thickness of AlMgB thin films has a value of 1.4 μm at the negative bias voltage of 100 V. With the increase of the negative bias voltage, the thickness decreases

Table 1 Deposition parameters of AlMgB thin films by magnetron sputtering

Parameters	Values
Base pressure	7.0×10^{-4} Pa
Working pressure	5.0×10^{-1} Pa
Ar gas flow rate	8 sccm
Deposition time	2 h
DC power of Al target	20 W
RF power of Mg target	30 W
RF power of B target	600 W
Substrate temperature	200°C
Negative bias voltage	−100 to −400 V
Duty cycle	10.5%
Frequency	40.5 kHz

down to nearly 0.6 μm at the negative bias voltage of 400 V. The decrease in thickness is related to the increased energy of the bombarding ions, U_k. Considering other deposition parameters, U_k is determined by[19]

$$U_k \propto \frac{D_w V_s}{P_g^{0.5}},$$

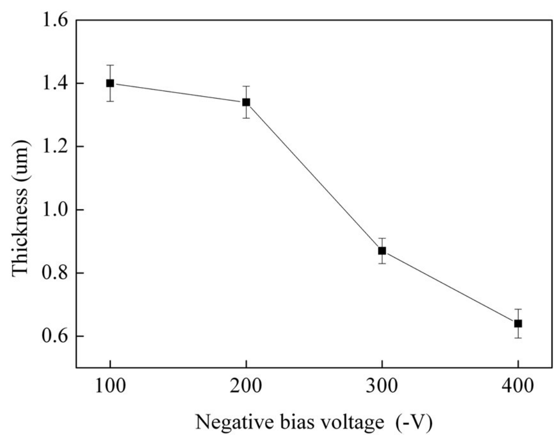
where D_w is the target power density, P_g is the process pressure and V_s is the negative bias voltage. During the deposition process, D_w and P_g remain constant, which indicates that U_k is directly proportional to V_s. Therefore, with the increase of negative bias voltage, the positive ions in the plasma around substrates are accelerated to the surface of substrates. These accelerated ions can deliver more energy to the depositing film, enhance the migration ability of the atoms on the growing film surface and lead to more ion bombardment. This results in re-sputtering of deposited film,[20] i.e. kicking off the adatoms or growing surface by the incoming ions,[21] and consequently hinders the increase of the thickness of the film.

SEM analysis

SEM micrographs of fractured cross-section of the AlMgB thin films are illustrated in Fig. 2. The decrease in thickness of the deposited films caused by the increase of negative bias voltage can be seen obviously; this is coincident with the results measured by the surface profiler, shown in Fig. 1. Moreover, all deposited thin films are very homogeneous and smooth, and the AlMgB thin films depict the thinnest microstructure with a well-attached interface at a negative bias voltage of 400 V. We speculate that the increase of negative bias voltage may increase the density of deposited thin films, which contributes to improve the hardness of thin films. A detailed discussion of hardness of deposited films will be presented at the end of this paper.

AFM analysis

Figure 3 displays the evolution of the AFM surface morphology of the AlMgB thin films (on $4 \times 4\ \mu m^2$ area) for different negative bias voltages. It is found that the morphology of the films deposited at the negative bias voltage of 100 V is rather coarse, i.e., many particles like high hillocks and islands with large sizes distributed randomly on



1 Thickness of deposited AlMgB thin films as a function of the negative bias voltage

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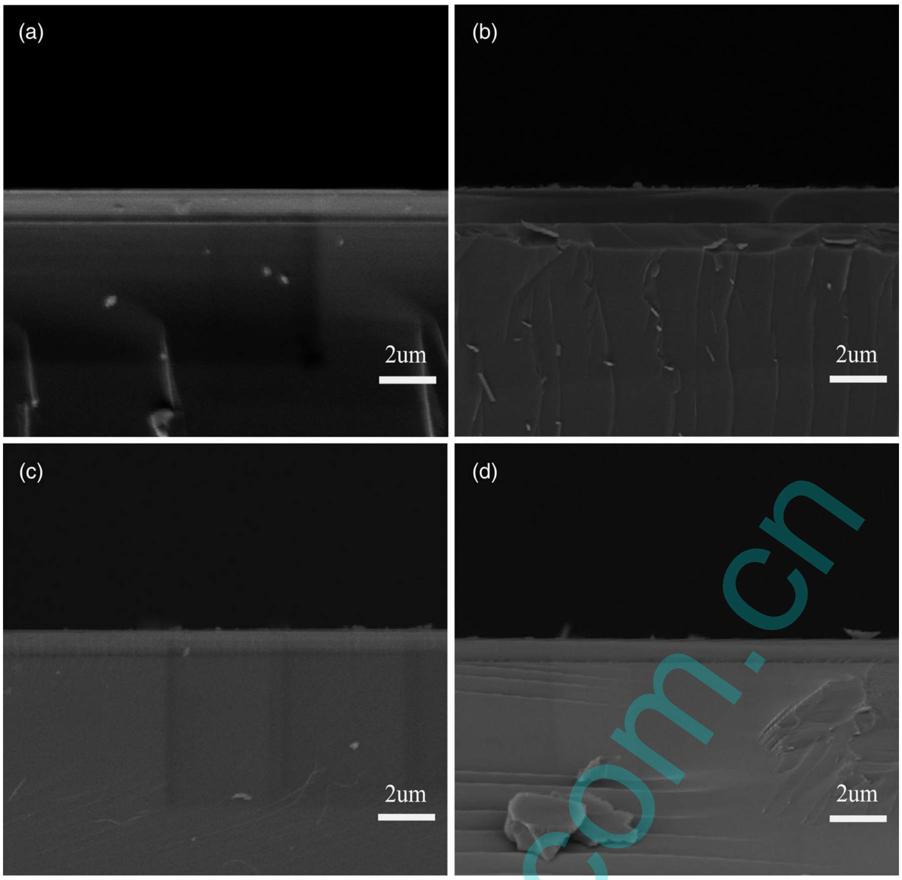
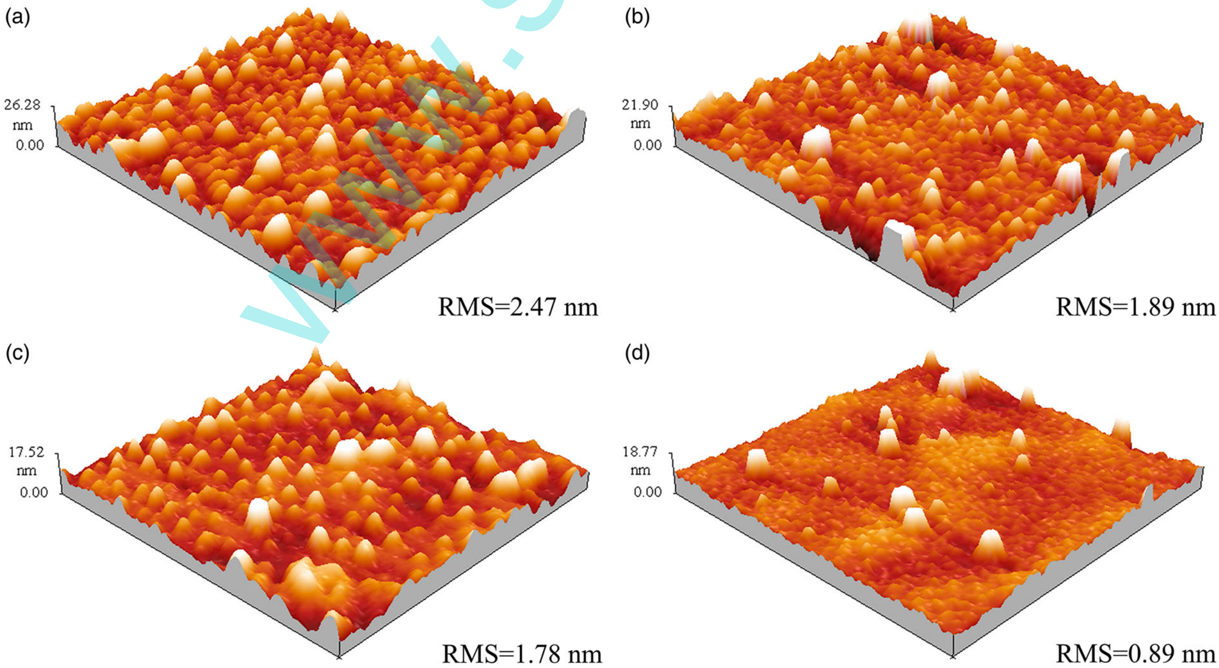


2 SEM micrographs of the cross-section of the deposited AlMgB thin films at different negative bias voltages: *a* 100 V, *b* 200 V, *c* 300 V and *d* 400 V

the surface and the particles are arranged loosely. However, with the increase of the negative bias voltage, the particles gradually become finer and finer, and the deposited films are more compact and denser. The surface of the deposited AlMgB thin films is quite smooth and uniform at the negative bias voltage of 400 V. This phenomenon can be explained as follows. With the increase of the negative bias voltage, the energy of positive ions increases. This



3 Three-dimensional AFM surface morphologies of AlMgB thin films deposited at different negative bias voltages: *a* 100 V, *b* 200 V, *c* 300 V and *d* 400 V

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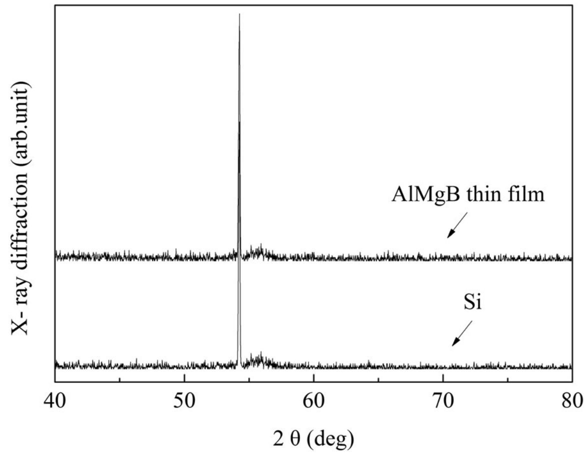
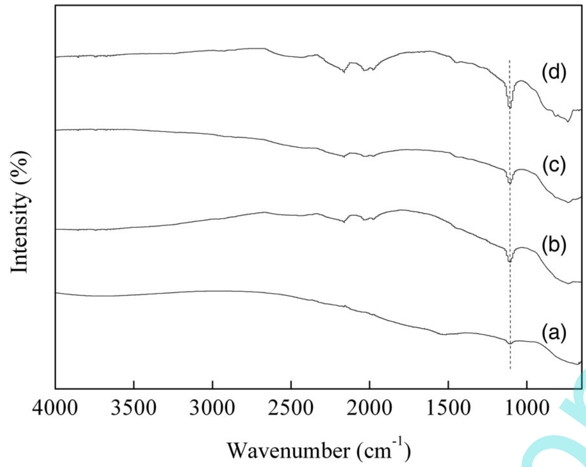


4 XRD patterns of AlMgB thin films deposited on Si wafer at the negative bias voltage of 400 V and silicon substrate



5 Infrared reflectance spectra of AlMgB thin films at different negative bias voltages: *a* 100 V, *b* 200 V, *c* 300 V and *d* 400 V

leads to a stronger interaction between the ions and the surface of the films, which promotes the diffusion of adatoms along the surface and in the films, and consequently forms a relative smooth surface.[22] Moreover, with the increase of the negative bias voltage, the roughness value of the deposited film surface also decreases and reaches 0.89 nm (atomically smooth surface) at the negative bias voltage of 400 V. This variation can be also ascribed to the enhanced preferential sputtering of the higher micro-asperities on the surfaces, due to higher electric field on their top.[23]

XRD analysis

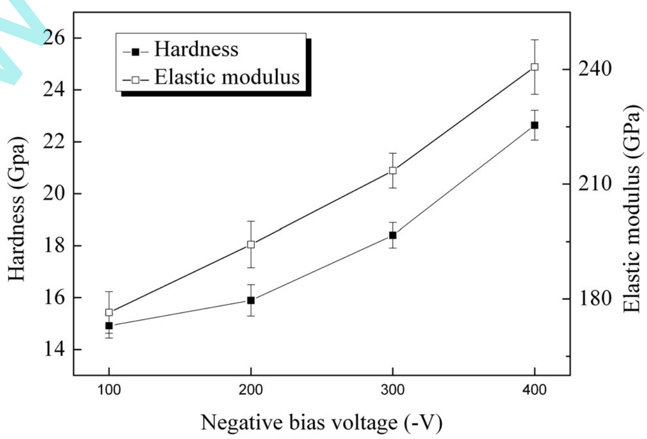
The X-ray diffraction patterns of the AlMgB thin films at different negative bias voltages are almost the same. Thus, for convenience, we only show the XRD patterns of the AlMgB thin films at the negative bias voltage of 400 V in Fig. 4, along with a spectrum of silicon substrate for comparison. As shown, there is almost no obvious diffraction peak corresponding to the AlMgB thin films, except for one around 52°, which is the characteristic of the silicon substrate plane. This indicates that our deposited AlMgB thin films are X-ray amorphous. In conclusion, the amorphous structure of the AlMgB thin films is nearly not affected by the increase of the negative bias voltage, i.e., the amorphous structure of the AlMgB thin film remains stable.

FTIR spectra

To further study the structural characteristics of AlMgB thin films, the FTIR of the AlMgB thin films for different negative bias voltages are recorded and shown in Fig. 5. As can be seen, all the samples have an absorption band centred at 1100 cm^{-1}, which can be ascribed to the F_{1u} vibrational mode of a single B_{12} icosahedron.[24] The absorption band is very weak at the negative bias voltage of 100 V, which indicates that the B_{12} icosahedron is not fully developed at low negative bias voltage. However, with increasing the negative bias voltage, the absorption intensity become stronger, which denotes that more well-formed B_{12} icosahedra appear in our deposited AlMgB thin film at higher negative bias voltage.

Hardness analysis

Figure 6 shows the hardness and elastic modulus of the AlMgB thin films as a function of negative bias voltage. As can be seen, the hardness of the AlMgB thin films is only 15 GPa at the negative bias voltage of 100 V. However, with the increase of the negative bias voltage, it increases rapidly up to 22.6 GPa at the negative bias voltage of 400 V. The variation of the elastic modulus with



6 The hardness and elastic modulus of deposited AlMgB thin films as a function of negative bias voltage

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the increase of negative bias voltage has a similar trend, which reaches 240 GPa at the negative bias voltage of 400 V. These two variation behaviours with the negative bias voltage can be explained as follows. There exist many factors for the hardness enhancement of AlMgB thin films. The increasing of density and the content of B_{12} icosahedra with the increasing of negative bias voltage are major factors. Just as discussed in sections SEM and AFM analysis, in the co-sputtering process, with the increase of the negative bias voltage, more energetic ions bombard to the surface of growing thin films, which can deliver more energy to the depositing films, promoting the mobility of adatoms. At the same time, these energetic ions can kick off and replace the poorly absorbed adatoms. Consequently, the deposited films become dense. In addition, in the AlMgB thin films, the Al and Mg atoms connecting to the B_{12} icosahedra donate an electric charge and thus improve the strength of the boron bonds. At high negative bias voltage, as discussed in the section of FTIR spectra, more well-formed B_{12} icosahedra are presented in AlMgB thin films. Both these contribute to the hardness of AlMgB thin films. It is worth mentioning that the AlMgB thin films obtained at a high bias voltage have a good adhesion to substrate up to now, which can adhere to the substrate for more than one year.

Conclusion

In conclusion, amorphous AlMgB thin films were successfully prepared by the magnetron sputtering system. The bias effects on the AlMgB thin films were discussed in detail and a good AlMgB thin film was obtained at a high negative bias voltage. This exploration of bias effects is valuable to fill the investigation of AlMgB thin films and lay the foundation for engineering application. The AlMgB thin films prepared at a high negative bias voltage were found to be generally dense and containing more well-formed B_{12} icosahedra. These characteristics contribute to the hardness of the deposited films, which can reach 22.6 GPa and the corresponding elastic modulus is 240 GPa at the negative bias voltage of 400 V. These hard films have a roughness value of 0.89 nm, which is an atomically smooth surface. However, the AlMgB thin films prepared at low negative bias voltages exhibit a loose microstructure, coarse surface and contain few B_{12} icosahedra. Therefore, we conclude that the increase of the negative bias voltage can produce an improvement in film density, surface morphology and mechanical properties of the AlMgB thin films.

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