Deposition and characterization of AlMgB14 thin film coatings

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Deposition and characterization of AlMgB$_{14}$ thin film coatings

by

Yun Tian

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

Program of Study Committee:
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Signature was redacted for privacy.

Major Professor

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For the Major Program
To my grandmother, and my parents
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ABSTRACT

Boron-rich borides are a special group of materials possessing complex structures typically comprised of $\text{B}_{12}$ icosahedra. All of the boron-rich borides sharing this common structural unit exhibit a variety of exceptional physical and electrical properties. In this work, a new ternary boride compound $\text{AlMgB}_{14}$, which has been extensively studied in bulk form due to its novel mechanical properties, was fabricated into thin film coatings by pulsed laser deposition (PLD) technology. The effect of processing conditions (laser operating modes, vacuum level, substrate temperature, and postannealing, etc.) on the composition, microstructure evolution, chemical bonding, and surface morphology of $\text{AlMgB}_{14}$ thin film coatings has been investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), atomic force microscopy (AFM) and Fourier transform infrared (FTIR) spectrometry; the mechanical, electrical, and optical properties of $\text{AlMgB}_{14}$ thin films have been characterized by nanoindentation, four-point probe, van der Pauw Hall measurement, activation energy measurement, and UV-VIS-NIR spectrophotometer.

Experimental results show that $\text{AlMgB}_{14}$ films deposited in the temperature range of 300 K - 873 K are amorphous. Depositions under a low vacuum level ($5 \times 10^{-5}$ Torr) can introduce a significant amount of C and O impurities into $\text{AlMgB}_{14}$ films and lead to a complex oxide glass structure. Orthorhombic $\text{AlMgB}_{14}$ phase cannot be obtained by subsequent high temperature annealing. By contrast, the orthorhombic $\text{AlMgB}_{14}$ crystal structure can be attained via high temperature-annealing of $\text{AlMgB}_{14}$ films deposited under a high vacuum level ($< 3 \times 10^{-6}$ Torr), accompanied by strong texture formation. Low vacuum level-as deposited $\text{AlMgB}_{14}$ films have low hardness (10 GPa), but high vacuum level-as
deposited AlMgB₁₄ films exhibit an extremely high hardness (45 GPa - 51 GPa), and the higher deposition temperature results in still higher hardness. Furthermore, a very low friction coefficient (0.04 - 0.05) has been observed for high vacuum level-as deposited AlMgB₁₄ films, which could be ascribed to the in situ formation of a surface self-lubricating layer. Unlike most boron-rich boride films, high vacuum level-as deposited AlMgB₁₄ films also possess a low n-type electrical resistivity, which is a consequence of high carrier concentration and moderate carrier mobility. The operative electrical transport mechanism and doping behavior for high vacuum level-as deposited AlMgB₁₄ films are discussed in detail in this thesis.
CHAPTER 1. INTRODUCTION

The intermetallic compound AlMgB₁₄ is a boron-rich boride material possessing complex crystal structures typically comprised of B₁₂ icosahedra. AlMgB₁₄ exhibits a variety of outstanding properties: high melting temperature, extraordinary hardness, high electrical conductivity, low density, and excellent chemical inertness. The purpose of this research is to fabricate and characterize various AlMgB₁₄-based thin film coatings for a wide range of potential applications in microelectromechanical system (MEMS), microelectronic devices, and cutting tools.

This dissertation is organized into seven chapters and one appendix. Chapter 1 (this chapter) states the objective of the research and provides a brief summary of the studies that are presented in other chapters. Chapter 2 is a literature review providing background information on the previous research and recent development of boron-rich boride materials with the emphasis on their crystal structures, electronic structures and electrical properties. Chapter 3, a paper published in Thin Solid Films, reports the experimental investigations of microstructure and nanomechanical properties of thin films synthesized from an AlMgB₁₄/TiB₂ target in a pulsed laser deposition (PLD) system with mediocre vacuum level. This paper discusses the effects of high O impurity level caused by contaminants in the vacuum atmosphere on microstructure, crystallization behavior, and nanohardness of Al-Mg-B-Ti films. Chapter 4, a paper published in the Journal of Vacuum Science and Technology A, presents experimental studies of the fabrication of Al-Mg-B thin films by a high vacuum PLD system. The effects of processing conditions on composition, microstructure evolution, and surface morphology of the Al-Mg-B films are discussed in this chapter. Chapter 5, a paper published in Applied Physics Letters, deals with the production of superhard and self-
lubricating AlMgB$_{14}$ films as a potential protective coating for MEMS components working in oxidizing, corrosive, and/or high temperature environments. Chapter 6, a paper submitted to *Applied Physics Letters*, describes the electrical transport properties of semi-conducting AlMgB$_{14}$ films. The effects of deposition temperature on the electrical properties (electrical conductivity, charge carrier density, and Hall mobility) and electrical transport mechanism of AlMgB$_{14}$ films are discussed. Chapter 7 summarizes the general conclusions drawn from this body of research, and suggests future work that could yield AlMgB$_{14}$ films with novel microstructures and extraordinary properties.

One appendix is attached. This appendix describes the principles of X-ray photoelectron spectroscopy (XPS) technique, an important surface analysis method frequently used in this research. In addition, the procedures for obtaining spectra and data interpretation are presented briefly in this appendix.
CHAPTER 2. LITERATURE REVIEW

Boron-rich borides are a special group of materials possessing complex structures typically comprised of B_{12} icosahedra. All of the boron-rich borides sharing this common structural element exhibit a variety of outstanding properties: high melting temperature, extraordinary hardness, low density, and excellent chemical inertness. These properties make them suitable for engineering applications under conditions that are beyond the performance limits of most other materials. Boron-rich borides are also semiconductors with unique electronic properties that are essentially determined by the B_{12} icosahedra. Some properties of particular interest are: the Jahn-Teller effect in the B_{12} icosahedra [1]; the presence of intrinsic traps in the band gap induced by electron-phonon coupling [2,3]; the correlation between electron deficiency and structural defects [4]; the soliton-type transport behavior of electrons and holes [5, 6]; the electronic interaction between foreign atoms and the B_{12} icosahedra [7]; the long lifetime of electrons under specific conditions; and the high Seebeck coefficients at high temperatures [8]. During the past decade, boron-rich borides have attracted increasing attention due to their novel mechanical, thermal, and electrical properties. The following sections provide a review of the various aspects of boron-rich borides in terms of their crystal structures, electronic structures and electrical properties.

2.1 Crystal structures of boron-rich borides

2.1.1 \( \alpha \)-Rhombohedral Boron

The simplest structure of boron-rich borides is the \( \alpha \)-rhombohedral modification of elementary boron and related binary compounds (Figure 2.1). Each vertex of the rhombohedral unit cell is occupied by one B_{12} icosahedron, and additional atoms can be
accommodated on the main diagonal of the unit cell, forming three-atom chains (e.g., in boron carbide), bonded atoms in pairs (e.g., in B_{12}P_{2}, B_{12}As_{2}, B_{2.89}Si), and noninteracting atoms in pairs (e.g., in B_{6}O, B_{6}Be, B_{6}S) [9]. The only exception is Al atoms, which are accommodated in sites off the main diagonal [10]. The arrangement of these additional atoms leads to possible compositional and structural variety that is far from being exhausted by the research performed to date.

Figure 2.1. Unit cell of boron carbide (α-rhombohedral boron structure) [8].
2.1.2 β-Rhombohedral Boron

β-rhombohedral boron is the high-temperature equilibrium crystalline modification of elementary boron. As shown in Figure 2.2, β-rhombohedral boron has 105 atoms per unit cell [11]. The structural formula \((B_{12})_4(B_{28})_2B\) exhibits four \(B_{12}\) icosahedra (one positioned at the vertex and three occupy the edge centers of the unit cell), two \(B_{28}\) units arranged symmetrically with respect to a central single boron atom on the main diagonal of the unit cell.

Figure 2.2. Unit cell of β-rhombohedral boron.
The structural diversity of \( \beta \)-rhombohedral boron is specifically determined by the different holes in its boron framework, which are large enough to incorporate foreign atoms up to certain solubility limits. Numerous binary and ternary compounds have been prepared with Li, Mg, Al, Ga, Si, Ge, Cu, Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mn, Fe, Co, and Ni atoms.

2.1.3 \( \alpha \)-Tetragonal Boron

The unit cell of \( \alpha \)-tetragonal boron consists of 50 atoms (Figure 2.3) [12], which are arranged in four \( \text{B}_{12} \) icosahedra with one of their fivefold axes parallel to the \( c \) axis, two remaining single boron atoms are located at \((0, 0, \frac{1}{2})\) and \((\frac{1}{2}, \frac{1}{2}, 0)\).

\[ \text{Figure 2.3. Unit cell of } \alpha \text{-tetragonal boron [12].} \]
2.1.4 Orthorhombic Borides (AlMgB\textsubscript{14} type)

There are 64 atoms in one unit cell of orthorhombic borides (Figure 2.4) \[13\], in which B\textsubscript{12} icosahedra are packed in a distorted hexagonal arrangement, the metal atoms are accommodated in large holes outside the B\textsubscript{12} icosahedra and are rather weakly bonded to the boron framework. The structural formula is \((\text{B}^{1})\text{Me}(1)\text{Me}(2)\text{B}^{6}\) however, in most cases the metal sites are not completely occupied. Similar to the \(\alpha\)-rhombohedral boron, there are only B\textsubscript{12} icosahedra and single boron atoms in the structure.

2.1.5 Amorphous Boron

B\textsubscript{12} icosahedra are statistically distributed in amorphous boron. It has been shown that the short-range order and the medium-range order of amorphous boron are closely related to those of crystalline \(\beta\)-rhombohedral boron \[14,15\]. Accordingly, the external bonds of the B\textsubscript{12} icosahedra in amorphous boron are largely saturated covalently. Therefore, it seems likely that the electronic properties are closely related to those of \(\beta\)-rhombohedral boron as well, moreover, there may be a greater amount of holes in the amorphous structure to allow accommodating foreign atoms to modify the properties, which would be very favorable for engineering applications, because well-established techniques can be used to prepare amorphous materials readily, for example, in thin film deposition.
Figure 2.4. Crystal structure of orthorhombic AlMgB$_{14}$. (a) Projection on the $ab$ plane. (b) Projection on the $bc$ plane.
2.2 Electronic structures of boron-rich borides

2.2.1 Common electronic behaviors of boron-rich borides

- Boron-rich borides are $p$-type semiconductors, overcompensation to $n$-type demands donor densities of the order of $10^{20}$ cm$^{-3}$ [16].
- The band gaps of boron-rich borides are independent of the crystal structures [16].
- A split-off valence band of 0.19 eV above the valence band edge has been found in many boron-rich borides.
- The electronic transport in boron-rich borides is determined by hopping with an activation energy of about 0.2 eV [5, 6].

2.2.2 $B_{12}$ Icosahedron and Its Orbitals

Theoretical calculations on the regular $B_{12}$ icosahedron show that the electronic configuration $2s^22p^1$ for ground state B atom is hybridized to $2s^12p_x^12p_y^1$ with 3 electrons available for bonding [17]. There are 25 bonding orbitals in a regular $B_{12}$ icosahedron, which are occupied by 36 electrons; in addition, there are 23 empty antibonding orbitals. If the external bonds are assumed to be covalent, then the electrons are distributed in such a manner that there are 12 electrons occupying 12 orbitals of external bonds and the other 24 electrons occupy 13 orbitals of intraicosahedral bonds. This electron-deficient structure leads to the intraicosahedral multiple-center bonds in $B_{12}$ icosahedron, which is stable in spite of lacking two electrons [18].

The $B_{12}$ icosahedra in boron-rich borides were found to be slightly distorted, this distortion has been attributed to the Jahn-Teller effect [1], which generally occurs in the crystal structures with high symmetry where the orbit-degenerated electronic states couple with asymmetrical vibrations. It was shown by group theory that the icosahedral point group
$I_h$ is reduced to the subgroup $D_{3d}$ by this distortion [19], and the molecular orbitals of B$_{12}$ icosahedra are affected by this distortion as well. Comparison of the character tables of $I_h$ and $D_{3d}$ shows the splitting of all the three-, four- and five-fold degenerated irreducible representations of the $I_h$ group, because they are not allowed in the $D_{3d}$ group (Figure 2.5). The uppermost four-fold degenerated $G_u$ orbital of the regular B$_{12}$ icosahedron partially occupied by six electrons is thus split so that occupied and unoccupied orbitals become separated.

![Diagram of orbitals](image_url)

**Figure 2.5.** Jahn-Teller induced splitting of the icosahedral orbitals, the symmetry is reduced from $I_h$ (free icosahedron) to $D_{3d}$ (icosahedron in rhombohedral crystal structure) [1].
The discrete bonding orbitals of single B$_{12}$ icosahedron spread to energy bands in boron-rich borides. Since the external bonding is stronger than the intraicosahedral one, the orbitals of external bonds are lower in energy and do not make contribution to the uppermost portion of the valence band, thus the intraicosahedral bonds prevail in this energy range. Occupied and unoccupied intraicosahedral bonding states are energetically separated due to Jahn-Teller induced splitting, accordingly, semiconductor behavior results in spite of the odd number of electrons in a boron atom.

2.2.3 Energy Band Structure of $\beta$-Rhombohedral Boron

Figure 2.6 illustrates the electronic structure of $\beta$-rhombohedral boron [20], which is typical for all the boron-rich boride materials. The band gap is characterized by an indirect allowed interband transition. The valence band consists of an upper split-off subband VB$_1$ and a lower subband VB$_2$. VB$_1$ is generated by the Jahn-Teller distortions of the B$_{12}$ icosahedra as described above, such effect only occurs on the B$_{12}$ icosahedra at the vertex of the unit cell, and hence the density of states of VB$_1$ is relatively low [21], which plays an important role in the electrical transport process of boron-rich boride materials. Optical transitions from the lower VB$_2$ to the upper VB$_1$ are forbidden. In thermal equilibrium, the Fermi level is positioned within the upper subband VB$_1$. Moreover, strong electron-phonon coupling in B$_{12}$ icosahedra leads to the formation of six intrinsic high-density trap levels in the band gap [2]. The generation of these intrinsic trap levels requires free electrons in the conduction band and the excitation of the intraicosahedral phonons as well. The involved phonons are antisymmetric breathing F$_{1u}$ mode and F$_{2u}$ mode of the B$_{12}$ icosahedron and the symmetry axes of the atom displacement are the six fivefold symmetry axes of the B$_{12}$ icosahedron, therefore the electrons can interact with up to six pairs of phonons to yield the
six intrinsic trap levels in the band gap. Electrons cannot be directly excited from the valence band into these trap levels because these levels do not exist without trapped electrons. Recombination of trapped electrons with the holes in valence band needs pre-excitation of these electrons into the conduction band.

Figure 2.6. Electronic structure of $\beta$-rhombohedral boron [20].
2.3 Electrical transport mechanism of boron-rich borides

Based on the special electronic structure of boron-rich boride materials, the following electrical transport mechanism has been proposed: When the thermal energy is sufficient, the upper valence band VB₁ is partially occupied by electrons in low-density localized states; these electrons are thermally excited from the nonicosahedral structure elements and/or the lower valence band VB₂ with free holes left behind, thus VB₁ acts like an intrinsic acceptor level in nature. Consequently, two electrical transport mechanisms are operative simultaneously in principle: low-mobility hopping conduction at the Fermi level within the upper valence band VB₁ and high-mobility band-type conduction by free holes in the lower valence band VB₂. This prediction has been proved by the experimental investigations of dynamical conductivity of the boron carbide (Figure 2.7) [20]. At substantially high temperatures, electrons can be excited from the lower valence band VB₂ into the conduction band directly. However, due to the presence of electron traps with high density of states in the band gap, the contribution from conduction electrons to the charge transport is extremely low even though they probably have a smaller effective mass. Because of the complex electrical transport behaviors exhibited by boron-rich boride materials, it would be difficult to reliably determine their carrier mobility. The carrier mobility of the boron-rich boride materials also depends on the methods of measurement. For example, at high frequencies the carriers with band-type mobility dominate, whereas at low frequencies the carriers with hopping mobility prevail. Characteristic carrier mobility determined by the transit times of optically excited electrons and holes is: \( \mu_e = 0.11 \text{ cm}^2\text{V}^{-1}\text{S}^{-1} \) and \( \mu_h = 0.076 \text{ cm}^2\text{V}^{-1}\text{S}^{-1} \) [6].
2.4 Doping behaviors of boron-rich borides

The doping of semiconductors to change their conductivity characteristics is a fundamental requirement for the technical applications. In the case of boron-rich boride materials, this has been done successfully by the interstitial accommodation of Fe atoms in the $\beta$-rhombohedral boron structure [22]. Ni, Cr, and V have been found to be effective
donors leading to n-type conductivity in $\beta$-rhombohedral boron as well. The highest negative Seebeck coefficient has been realized in $\beta$-rhombohedral boron doped with vanadium [23].

According to the band structure of $\beta$-rhombohedral boron, n-type conductivity can only be obtained when the unoccupied states in the valence band and the intrinsic electron trap levels are filled by electrons originating from donor states positioned above the uppermost trap level. This has been confirmed by Mössbauer investigations where the degree of ionization was determined for Fe atoms accommodated in the interstitial A and D sites of the $\beta$-rhombohedral boron [7], as presented in Figure 2.8. The special electronic structures of boron-rich borides make them insensitive to impurities at concentrations that would significantly change the electronic properties of conventional semiconductors. Doping can be achieved only at much higher concentration levels. Hence it is easier and less expensive to prepare boron-rich boride-based semiconductors than the conventional semiconductors, where extremely high purity level is required.

2.5 Structural defects in boron-rich borides

The structural defects have not been taken into consideration in the former discussions of boron-rich boride materials. However, thorough investigations of crystal structures of boron-rich borides indicate that there exist an appreciable amount of well-defined defects in the form of incomplete occupations of the atomic sites and/or antisite defects, this suggests that the defects are fundamental characteristics associated with the icosahedral boron-rich borides [4]. Examples of such defects are listed as follows:
• α-rhombohedral boron structure (B\textsubscript{12}X\textsubscript{2} or B\textsubscript{12}X\textsubscript{3}): unoccupied atomic sites (vacancies) in the chains [24]. Such defect concentration can be as high as 9.3 at.% in B\textsubscript{13}C\textsubscript{2}.

• β-rhombohedral boron structure: unoccupied boron sites (lack of 1.7 boron atoms per unit cell). This leads to an intrinsic point defect density of about 4.9 defects per unit cell [25].

• Orthorhombic AlMgB\textsubscript{14} type structure: unoccupied metal sites, and possibly unoccupied non-icosahedral boron sites.

![Figure 2.8. Seebeck coefficient of β-rhombohedral boron versus charge transfer from the Fe atoms to the icosahedral boron framework.](image-url)
References


Boron, Borides and Related Compounds (University of Duisburg, Duisburg, 1987), p.132.


CHAPTER 3. MICROSTRUCTURE AND NANOMECHANICAL PROPERTIES OF Al-Mg-B-Ti FILMS SYNTHESIZED BY PULSED LASER DEPOSITION


ABSTRACT

Thin films were deposited from an ultra-hard, nanocomposite AlMgB_{14}/TiB_{2} target on Si (100) by nanosecond (ns) and femtosecond (fs) pulsed laser deposition (PLD) techniques. X-ray diffraction was used to determine the film structure, and x-ray photoelectron spectroscopy was performed to examine the film compositions and chemical bonding states of constituents. The mechanical properties of thin films such as hardness and elastic modulus were determined by nanoindentation tests. Results showed that the as-deposited films were amorphous, possessing a complex oxide glass structure, and this structure was stable up to 1223 K. The preferential reaction of Al, Mg, and B with O inhibits the formation of crystalline AlMgB_{14}. The absence of B-B bonds and nanocrystalline structure leads to nanohardness values for as-deposited films as low as about 10 GPa. The intrinsic hardness of the film could not be evaluated exactly because of surface roughness and substrate effects.

INTRODUCTION

The intermetallic compound AlMgB_{14} was first studied more than 30 years ago, and it has been the subject of renewed interest due to its extreme hardness and high chemical stability [1,2]. The hardness of AlMgB_{14} containing 5 to 30 mol% additives lies in the range
35-46 GPa, which is comparable to the hardness of cubic-BN. The AlMgB\textsubscript{14} materials are lighter than the other ultra-hard materials. Additionally, the cost of AlMgB\textsubscript{14} is projected to be about five to ten times lower than costs of cubic-BN and diamond.

The crystal structure of AlMgB\textsubscript{14} is a body-centered orthorhombic arrangement, space group Ima\textsubscript{3}, \(a = 0.5848\) nm, \(b = 0.8112\) nm, \(c = 1.0312\) nm \[3,4\]. The unit cell contains 64 atoms and is based on four B\textsubscript{12} icosahedral units, the icosahedra are centered at (0, 0, 0), (0, 0.5, 0.5), (0.5, 0, 0), and (0.5, 0.5, 0.5), while the remaining eight B atoms lie outside the icosahedra, bonding to the icosahedral B atoms and to the intericosahedral Al atoms occupying a four-fold position at (0.250, 0.750, 0.250) and the intericosahedral Mg atoms occupying a four-fold position at (0.250, 0.359, 0). The B\textsubscript{12} icosahedra are arranged in distorted, close-packed layers. AlMgB\textsubscript{14} single crystals were prepared by a flux growth technique in the initial research \[3\], the microhardness of these AlMgB\textsubscript{14} crystals ranged from 26 to 28 GPa with a density of 2.59 g/cm\textsuperscript{3}. Recent study of AlMgB\textsubscript{14} involved fabrication using hot press sintering \[1\]. In this process, mechanical alloying is employed to comminute the elemental constituents into nanoscale powder. This powder is then consolidated at 1623 K to 1773 K under either vacuum or inert gas environments, producing a fully dense, ultra-fine grained microstructure. Chemical additives such as Si and TiB\textsubscript{2} were found to increase hardness significantly, placing this material in the super-hard category.

Crystallographic studies indicate that the metal sites are not fully occupied in the AlMgB\textsubscript{14} lattice, so that the true stoichiometry may be Al\textsubscript{0.75}Mg\textsubscript{0.75}B\textsubscript{14} \[3,4\]. Theoretical studies indicate the unoccupied metal sites are the necessary consequence of the deficiency of electrons in the valence band \[5\]. In addition, these icosahedral borides exhibit higher electrical conductivity (~ 80 to 1500 \(\Omega^{-1}\text{m}^{-1}\)) than traditional hard materials and show
hopping conduction even in high-purity crystals [6]. Recent band structure calculations [7] performed on these borides suggest that the hardness may change as the nature of the electronic states at the Fermi level change, hence it appears that doping may play a vital role in determining the physical properties. The AlMgB$_{14}$ single crystals show p-type semiconducting behavior and can be overcompensated to n-type by doping with a variety of different metal atoms [8]. More recently, dry machining tests in which bulk AlMgB$_{14}$ was used as the cutting tool, showed an unusual absence of tool heating, suggesting that this new family of ultra-hard materials might possess very low thermal conductivity. The novel mechanical and electronic properties combined with excellent thermal dissipative capability is attributed to a complex interplay between the interaction within each icosahedron (intrahedral bonding) and the interaction among the icosahedra (intericosahedral bonding) [1].

Due to its novel mechanical, electrical, and thermal properties, AlMgB$_{14}$ is a promising candidate for application in MEMS [9], microelectronic devices and cutting tools. AlMgB$_{14}$ thin films could be deposited by PVD on MEMS components such as microgear, microturbine, micromotor for wear-resistance and lubrication. AlMgB$_{14}$ thick films could be utilized as hard coatings for cutting tools [10]. To achieve greater fundamental understanding and control of the mechanical properties and microstructure of AlMgB$_{14}$ films, an investigation was undertaken to study the effects of processing and structures of AlMgB$_{14}$ films on their mechanical properties. The investigation of microstructure evolution in AlMgB$_{14}$ films and the relation between microstructure and mechanical properties was chosen as the primary focus of this research.
Among the several physical vapor deposition (PVD) techniques (e.g. thermal evaporation, sputtering, etc.), pulsed laser deposition (PLD) is perceived to be a good method to deposit AlMgB₁₄ films because of two unique characteristics [11]: 1) **Congruent ablation** - Rapid heating of the target and rapid cooling of the film on the substrate do not allow dissociation of source material, even though the constituents have different vapor pressures. This leads to stoichiometric films of complex, multicomponent alloys. 2) **High kinetic energy species** - the ionized and excited species ablated by the laser have high kinetic energy (~200-1000 kT) and velocities, and thereby promote film crystallinity and dense packing at low temperature.

**EXPERIMENTAL PROCEDURE**

Pulsed laser deposition (PLD) experiments were performed in a vacuum chamber (5 × 10⁻⁵ Torr) using either a KrF excimer (23 nanosecond pulses) laser or a Ti: Sapphire (120 femtosecond pulses) laser. The target, prepared by uniaxial hot pressing, was AlMgB₁₄ (doped with 20 wt% TiB₂). The target contained some oxygen impurity in the form of Al₂MgO₄. The substrates were Si (100) wafers and carbon-coated copper grids. The substrate temperature was maintained at 773 K throughout the PLD process. The pulse energy was 250 mJ for ns-PLD and 0.1-0.5 mJ for fs-PLD. The spot area on the target was 1 mm² (ns-PLD) and 0.002 mm² (fs-PLD). After deposition, the samples were sealed in the quartz ampoule which was evacuated to 10⁻³ Torr and backfilled with He, then were annealed at different temperatures for different times. The experimental conditions are summarized in Table 3.1. The femtosecond laser was operated at a much higher repetition rate (1000 Hz).
than the nanosecond laser (5 Hz). The film thickness was measured by atomic force microscopy and weighing methods.

XRD patterns of thin films were collected using Cu Kα radiation with a Scintag x-ray diffractometer. X-ray photoelectron spectroscopy (Physical Electronics 5500 Multitechnique ESCA system) with monochromatic Al Kα radiation source (1486.6 eV) was used to determine the film compositions and the binding energies of core level electrons that reveal the chemical bonding states of Al, Mg, Ti, and B in the deposited films. Analysis spot size can be varied from $1 \times 0.8 \text{ mm}^2$ to $0.4 \times 0.4 \text{ mm}^2$ with energy resolution of less than 0.5 eV. The base pressure for the analyzer system was less than $3 \times 10^{-10}$ torr. The films were subjected to an Ar⁺ bombardment for 10 minutes to remove surface contamination before the XPS analysis.

Nanoindentation testing (CSEM Instruments, Inc.) with a Berkovich diamond indenter (a three-sided pyramid with an area-to-depth function the same as that of a Vickers indenter) was used to measure the hardness and elastic modulus of the films. In this test, the load was gradually increased to a pre-set maximum value such that both elastic and plastic deformation occurred in the thin film. The load was then released, causing partial or complete relaxation. The unloading was dominated by elastic displacements. Several measurements with different penetration depths were performed at the center and at the edge of the films. Nanohardness and modulus were obtained from the load-displacement curves based on the improved method [12]. First, the contact stiffness $S$ and the contact depth $h_c$ were determined from load-displacement curves. Second the hardness $H$ and the modulus $E$ were calculated from the following equations:
\[ H = \frac{P_{\text{max}}}{A_c} \quad \text{and} \quad \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu^2}{E} = \frac{2}{\sqrt{\pi}} \frac{\sqrt{A_c}}{S} \] (1)

where \( A_c \) is the projected contact area obtained from the contact depth, \( E_i \) and \( \nu_i \) are the modulus and Poisson's ratio of the indenter respectively, \( E \) and \( \nu \) are the modulus and Poisson's ratio of the tested sample.

Table 3.1. The experimental conditions for pulsed laser deposition of Al-Mg-B-Ti films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser</th>
<th>Pulse energy (mJ)</th>
<th>Repetition rate (Hz)</th>
<th>Deposition time (min.)</th>
<th>Annealing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ns</td>
<td>250</td>
<td>5</td>
<td>60</td>
<td>As-deposited</td>
</tr>
<tr>
<td>B</td>
<td>ns</td>
<td>250</td>
<td>5</td>
<td>60</td>
<td>1223 K, 2 hrs</td>
</tr>
<tr>
<td>C</td>
<td>ns</td>
<td>250</td>
<td>5</td>
<td>60</td>
<td>1323 K, 12 hrs</td>
</tr>
<tr>
<td>D</td>
<td>fs</td>
<td>0.5</td>
<td>1000</td>
<td>10</td>
<td>As-deposited</td>
</tr>
<tr>
<td>E</td>
<td>fs</td>
<td>0.5</td>
<td>1000</td>
<td>10</td>
<td>1323 K, 12 hrs</td>
</tr>
<tr>
<td>F</td>
<td>fs</td>
<td>0.3</td>
<td>1000</td>
<td>60</td>
<td>As-deposited</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Figure 3.1 (a) shows XRD patterns of ns-laser deposited films under different processing conditions (samples A, B, and C). The as-deposited film (sample A) exhibits a very broad peak around 20° 2θ diffraction angle, indicating that the structure is amorphous. The pattern for a film annealed at 1223 K (sample B) remains almost unchanged compared with the as-deposited film, implying that the amorphous structure of as-deposited film is stable up to 1223 K. The XRD pattern for 1323 K annealed film (sample C) shows two weak reflections around 20°, illustrating that some crystallization of the amorphous phase has
occurred. These peaks did not match with any diffraction lines of the AlMgB$_{14}$ orthorhombic structure, but might arise from new phases formed in this complex multicomponent system.

Figure 3.1 (b) shows XRD patterns of fs-laser deposited films under different processing conditions (samples D and E). The as-deposited film is amorphous. For the 1323 K annealed sample, an additional weak, broad peak is observed. This peak, which does not correspond to the AlMgB$_{14}$ structure, suggests new phase formation at this annealing temperature.

![Figure 3.1 (a) XRD patterns of ns-laser deposited films. (b) XRD patterns of fs-laser deposited films.](image)

Figure 3.2 shows B 1s XPS spectra for samples A and D. The peak at binding energy 188.08 eV was found to correspond to metal boride, probably TiB$_2$. Another peak at binding energy 191.63 eV for sample A and 191.88 eV for sample D was found to correspond to boron oxide; the absence of diffraction peaks for any boron oxide in the XRD patterns
suggests that B-O bonding was present only in the short-range order comprising the amorphous phase. Figure 3.3 (a) shows Al 2p XPS spectra and (b) Mg 2s XPS spectra for samples A and D. The presence of short-range Al-O bonding is revealed by the peak at a binding energy of 75.35 eV. No peaks of metallic Al were observed, indicating that the films contain no metallic Al. The peak at binding energy 90.85 eV for Mg 2s might be attributed to short-range Mg-O bonding. Figure 3.3 (c) shows Ti 2p XPS spectra for samples A and D. The peak at binding energy 460.63 eV corresponds to the $2p_{1/2}$ level, and the peak at binding energy 454.75 eV corresponds to the $2p_{3/2}$ level; thus, it is concluded that these peaks probably result from TiB$_2$, which is in agreement with the previous results. It should be noted that the resemblance of XPS spectra can be seen between samples A and D suggesting that the laser pulsing mode (nanosecond or femtosecond) has no substantial influence on the chemical bonding states of different constituents in the films.

![Figure 3.2. Boron 1s XPS spectra for sample A and D.](image-url)
The XRD results offer evidence that the films formed are amorphous and are stable up to 1223 K. According to the XPS spectra, the amorphous region in the films has an oxide glass structure in which various bondings of short-range order dominate with B playing the role of network former. XPS composition analysis shows that the oxygen concentration is 18.94 at.% and 18.36 at.% for sample A and D respectively, such high oxygen contamination results from the target typically containing 2 to 3 wt.% MgAl₂O₄ impurity, and the mediocre vacuum quality in the PLD chamber. Due to the presence of large amounts of oxygen, the
orthorhombic AlMgB\textsubscript{14} crystal structure could not be obtained even at annealing temperature as high as 1323K because the oxidation of Al, Mg and B was more thermodynamically favorable, promoting the formation of amorphous structure (B-O bond) in preference to B\textsubscript{12} icosahedra (B-B bond). Therefore much lower oxygen content in films may be necessary for formation of the orthorhombic AlMgB\textsubscript{14} phase. It was reported that B\textsubscript{12} icosahedra can be formed in boron suboxide B\textsubscript{22}O films with oxygen fractions of 1-15 at.% deposited by magnetron sputtering [13]. The difficulty in obtaining the same structure in the present study might be attributable to the incorporation of Ti in films that changes the composition ratio required for B\textsubscript{22}O stoichiometry.

Nanoindentation is crucial to studies of mechanical properties of thin films and ultra-thin films. The nanoindentation test is strongly affected by the surface roughness of the thin film [14]. In general, very smooth surfaces are required to obtain reliable contact stresses at small depths of indentation. Nanoindentation is also dependent on the penetration depth due to substrate effects, indentations with contact depths of less than 10-20% of the film thickness are recommended to ensure that the intrinsic properties of the film were not affected by the underlying substrate [15]. Sample F was chosen for the nanoindentation test because of its thicker film and much lower surface roughness, Si (100) with Knoop hardness 8.3 GPa was used as the substrate. The nanoindentation hardness and modulus of sample F, obtained from the edge and the center, are plotted in Figure 3.4, as a function of penetration depth. Both hardness and modulus decrease with increasing penetration depth exhibiting typical behavior of a hard film on a soft substrate. If the film is harder than the substrate, then most of the plastic deformation occurs in the soft substrate, leading to a “sink-in” effect even though the indenter is not yet through the film. The maximum hardness of \( \sim 10 \text{ Gpa} \) at
the center and ~ 6 Gpa at the edge was observed. Both hardness and modulus were lower at
the edge than at the center; this could be attributed to the nature of PLD in that the film
thickness decreases from the center to the edge as a cosine function, and the edge properties
might have included the more pronounced substrate effects. The average thickness of sample
F is about 1 µm, and the maximum penetration depth is 262 nm in the center and 357 nm at
the edge, so the hardness and modulus values measured at the center should be closer to the
intrinsic film properties.

The 10 Gpa hardness of the film measured in this work is much lower than the
microhardness of bulk AlMgB14. The hardness of single crystal AlMgB14 is about 28 Gpa
[16]; the hardness of hot-pressed AlMgB14 is about 32 Gpa, and the hardness of hot-pressed
AlMgB14 + TiB2 is about 38 to 46 Gpa [1]. The hardness of the film measured in this study
is much lower; this is probably due to the presence of the amorphous structure in which the
strong B-B bond is absent and the weaker B-O bond dominates. The absence of the
interfaces between the AlMgB14 and TiB2 phases may also contribute to this much lower
hardness. It has been reported [1] that the family of hot-pressed AlMgB14 materials derive
their extreme hardness by the effect of nanocrystalline multiphase structures, where
interfacial phenomena govern the strength. Veprek et al. [17] have reported extraordinarily
high hardness values in CVD nanocomposite thin films consisting of transition metal nitrides
as the first phase and amorphous Si3N4, BN, or TiSi_x as the second phase. None of these
compounds is intrinsically as hard as the nanocomposite, therefore Veprek et al. refer to the
microstructural contribution to hardness in these nanocomposites as “extrinsic hardness”. It
should be realized that the nanoindentation test is also strongly affected by the film thickness
and surface roughness as described above. For example, nanoindentation studies of TiN
films [14] showed lower and scattered hardness values at small penetration depths due to surface roughness, therefore the penetration depths must be high enough to make the measurements reliable. However, to minimize substrate effects the penetration depths have to be low enough to keep the indentation within 10-20% of film thickness [15]. In our case, the minimum penetration depth is 246 nm at the center, which is larger than 20% of the film thickness (1 μm). Hence the nanohardness value 10 Gpa may not exactly reflect the intrinsic property of the film because of the contribution from the substrate deformation.

CONCLUSIONS

Al-Mg-B-Ti films were synthesized by nanosecond and femtosecond pulsed laser deposition technique. The as-deposited films were amorphous. Significant crystalline phase formation occurred by subsequent annealing at 1323 K; however, the AlMgB$_{14}$ orthorhombic structure was not observed, which is thought to result from the high oxygen content in these films. Nanohardness of about 10 Gpa was observed for as-deposited films. This value is much lower than hardness measured in single crystal and hot-pressed polycrystalline AlMgB$_{14}$, probably due to the absence of B-B bonding and nanocrystalline microstructure. Surface roughness and substrate effects can contribute to inaccuracy of the nanoindentation measurement.
Figure 3.4. The penetration depth dependence of the hardness and modulus of sample F (center and edge).

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REFERENCES

CHAPTER 4. MICROSTRUCTURE EVOLUTION OF Al-Mg-B THIN FILMS BY THERMAL ANNEALING


ABSTRACT

The growth of Al-Mg-B thin films on SiO₂/Si (100) substrates was performed by nanosecond pulsed laser deposition (PLD) at three different substrate temperatures (300 K, 573 K and 873 K). The as-deposited films were then annealed at 1173 K or 1273 K for two hours. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and atomic force microscope (AFM) were employed to investigate the effects of processing conditions on composition, microstructure evolution and surface morphology of the Al-Mg-B films. The substrate temperatures were found to affect the composition of as-deposited films in that the Mg content decreases and C content increases at higher substrate temperatures, in particular for the 873 K-deposited film. XRD results show that the as-deposited films were amorphous, and this structure may be stable up to 1173 K. Annealing at 1273 K was found to fully crystallize the room temperature and 573 K-deposited Al-Mg-B films with the formation of polycrystalline orthorhombic AlMgB₁₄ phase, accompanied by the development of pronounced (011) preferred orientation. Nevertheless, high C incorporation in the 873 K-deposited Al-Mg-B film inhibits the crystallization and the amorphous structure remains stable even during 1273 K-annealing. The presence of Si in the room temperature-deposited 1273 K-annealed film due to the interdiffusion between substrate and film leads to the
formation of additional tetragonal $\alpha$-FeSi$_2$ phase, which is thought to cause the surface cracking and microstructural instability observed in this film.

**INTRODUCTION**

The novel mechanical, electrical, and thermal properties of boron-rich borides make them a productive object of study from both scientific and engineering perspectives. They are stable, refractory semiconductors, and fabrication of boron-rich boride-based electronic devices was recently reported.\(^1\)\(^2\) They possess large Seebeck coefficients and low thermal conductivity, which suggests possible use in thermoelectric energy conversion.\(^3\)\(^4\) Due to the large neutron capture cross section of $^{10}$B, boron-rich borides have found application in fission reactors for absorption of thermal neutrons and as solid-state neutron detectors.\(^5\)\(^6\)

Boron-rich borides also have been recognized for their high hardness, low density, and chemical inertness, which makes them attractive materials for cutting tools and wear-resistant coatings.\(^7\)\(^8\)

The basic structural feature of boron-rich borides is the B$_{12}$ boron icosahedral cluster, in which each boron atom shares three valence electrons with five neighboring boron atoms, leading to electron-deficient, three-center intraicosahedral bonding.\(^3\) These B$_{12}$ icosahedra are either linked directly to one another or are connected via single B or non-B atoms, forming a large variety of open frameworks, which distinguishes the boron-rich borides from conventional semiconductors with simple translational symmetry and from amorphous semiconductors with short-range order.

There has been considerable interest in studying boron-rich borides in thin-film form, especially B$_4$C, B$_4$N, and boron suboxide ($B_xO$, $x > 1$) for potential application as hard
coatings, due to their extraordinary mechanical properties. Boride films have been prepared by various deposition methods: ECR microwave plasma assisted thermal evaporation, hot filament chemical vapor deposition, reactive RF magnetron sputtering, pulsed DC magnetron sputtering, dual ion beam deposition, vacuum (cathodic) arc deposition, and pulsed laser deposition. Boride films obtained in prior work were usually amorphous, and the mechanical properties vary with different deposition techniques. Hardnesses of 25-30 GPa and elastic moduli of 180-300 GPa have been observed. Furthermore, oxidation at the free surfaces of these boride films tends to grow a glassy B2O3 layer, which reacts spontaneously with ambient water vapor to form a thin boric acid (H3BO3) boundary film. This boundary film can have a friction coefficient as low as 0.05, thus providing an excellent self-lubricant. For these reasons, boron-rich boride films are emerging as an intriguing new class of superhard materials with a wide range of applications.

Recently, a ternary boride AlMgB14 with extreme hardness and high thermal stability has been developed by Ames Laboratory scientists. The hardness of AlMgB14 with sub-micron-scale grain size ranges between 32 and 35 GPa, and the hardness of AlMgB14 containing 5 to 30 mol% additives lies in the range 35-46 GPa, with the highest hardness observed in material containing 30% TiB2 of mean phase size of ~200 nm. A hardness of 45 GPa is comparable to the hardness of cubic-BN (Table 4.1), placing this material in the super-hard category. Moreover, the cost of AlMgB14 is projected to be about five to ten times lower than the costs of cubic-BN and diamond. As shown in Figure 2.4, the crystal structure of AlMgB14 is a body-centered orthorhombic arrangement, space group Ima2, with lattice constants a = 0.5848 nm, b = 0.8112 nm, c = 1.0312 nm. The unit cell contains 64 atoms and is based on four B12 icosahedral units centered at (0, 0, 0), (0, 0.5, 0.5), (0.5, 0, 0),
and (0.5, 0.5, 0.5) within the unit cell, while the remaining eight B atoms lie outside the
icosahedra, bonding to the icosahedral B atoms and to the intericosahedral Al atoms
occupying a four-fold position at (0.250, 0.750, 0.250) and the intericosahedral Mg atoms
occupying a four-fold position at (0.250, 0.359, 0). Crystallographic studies indicate that
the metal sites are not fully occupied in the AlMgB₁₄ lattice, so that the true stoichiometry
may be Al₀.₇₅Mg₀.₇₈B₁₄, which is the necessary consequence of the electron deficiency in the
valence band. In addition, single crystal AlMgB₁₄ exhibits intrinsic n-type transport
behavior, and hot-pressed AlMgB₁₄ has higher electrical conductivity (∼ 80 to 1500 Ω⁻¹m⁻¹)
than most traditional hard materials. Recent band structure calculations performed on
these borides suggest that the hardness may change as the nature of the electronic states at the
Fermi level changes, hence it appears that doping may play a vital role in determining the
physical properties. More recently, dry machining tests in which bulk AlMgB₁₄ was used as
the cutting tool, showed an unusual absence of tool heating, suggesting that this
orthorhombic boride might possess very low thermal conductivity.
Its high hardness, high thermal stability, and desirable electrical and thermal properties
suggest potential utilization of AlMgB₁₄ as self-lubricating, wear-resistant and protective
coatings for cutting tools and mechanical components ranging in size from massive mining
and materials handling applications to MEMS. It was believed that the superhardness of
bulk AlMgB₁₄ is determined by its nanocrystalline multiphase structure since single crystal
AlMgB₁₄ has hardness of only 28 GPa. Veprek refers to this microstructural contribution to
hardness in the nanocomposite as “extrinsic hardness”. Thus, the appropriate crystalline
microstructure is thought to be crucial for achieving extreme hardness in thin film form.
However, no detailed investigations to date have been reported to study the deposition of

polycrystalline boride films, and the effect of processing conditions on the microstructure progression has not been fully addressed, therefore the primary focus of this research was devoted to preparing crystalline AlMgB\textsubscript{14} thin films and examining the influence of processing routes on composition, microstructure evolution and surface morphology of such films.

Table 4.1. Density and hardness of selected hard materials

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm\textsuperscript{3})</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (diamond)</td>
<td>3.52</td>
<td>70</td>
</tr>
<tr>
<td>BN (cubic)</td>
<td>3.48</td>
<td>45-50</td>
</tr>
<tr>
<td>SiC</td>
<td>3.22</td>
<td>24-28</td>
</tr>
<tr>
<td>TiB\textsubscript{2}</td>
<td>4.50</td>
<td>30-33</td>
</tr>
<tr>
<td>WC</td>
<td>15.72</td>
<td>23-30</td>
</tr>
<tr>
<td>TiC</td>
<td>4.93</td>
<td>28-29</td>
</tr>
<tr>
<td>Si\textsubscript{3}N\textsubscript{4}</td>
<td>3.19</td>
<td>17-21</td>
</tr>
<tr>
<td>AlMgB\textsubscript{14}</td>
<td>2.66</td>
<td>32-35</td>
</tr>
<tr>
<td>AlMgB\textsubscript{14} + Si</td>
<td>2.67</td>
<td>35-40</td>
</tr>
<tr>
<td>AlMgB\textsubscript{14} + TiB\textsubscript{2}</td>
<td>2.70</td>
<td>40-46</td>
</tr>
</tbody>
</table>

EXPERIMENTAL PROCEDURE

AlMgB\textsubscript{14} films were deposited on thermally oxidized Si (100) substrates by a turbo-pumped Neocera pulsed laser deposition (PLD) system (Figure 4.1). In this PLD system, a KrF excimer laser beam (\(\lambda = 248\) nm, pulse energy 70 mJ, pulse duration < 50 ns, repetition rate 10 Hz) was delivered to the hot-pressed baseline AlMgB\textsubscript{14} target with energy density of \(~1.2\) J/cm\textsuperscript{2} through a focusing lens to generate a plasma plume in a high vacuum chamber.
(typical base pressure $< 3 \times 10^{-6}$ Torr). The target contained some oxygen impurity in the form of MgAl$_2$O$_4$ spinel phase. The substrate was placed parallel to the target, and the distance between substrate and target was 7 cm. Depositions were carried out at three different substrate temperatures (room temperature, 573 K and 873 K), and the film thickness was controlled by the deposition rate of 0.014 Å/pulse and the total deposition time was 3 hours. After deposition, all as-deposited films were isothermally annealed at 1173 K or 1273 K for two hours, the annealing process was conducted in a NRC 2940 high temperature vacuum furnace, which was evacuated below a base pressure of $2 \times 10^{-6}$ Torr and then backfilled with yttrium gettered Ar to ambient pressure prior to annealing. The temperature ramp rate was set at 17°C/min.

X-ray diffraction (XRD) patterns of the films were collected using a Scintag 0-20 x-ray diffractometer with Cu K$_\alpha$ radiation. Surface topography and roughness of the films were studied using a Digital Instruments Dimension 3100 atomic force microscope (AFM) operated in tapping mode with a silicon pyramidal probe. The residual stresses of as-deposited films were determined by measuring the curvature of the film-substrate combination with AFM and using the Stoney formula:

$$\sigma_r = \frac{E_s d_s^2}{6R(1-\nu_s)d_f}$$

where $\sigma_r$ refers to the biaxial stress of the film, $E_s$, $\nu_s$, and $d_s$ are the Young's modulus, Poisson's ratio, and thickness of the substrate respectively; $d_f$ and $R$ are the film thickness and radius of curvature of the film-substrate composite. The film thickness was measured by AFM.
X-ray photoelectron spectroscopy (PHI™ Physical Electronics 5500 Multitechnique ESCA system) with monochromatic Al Kα radiation (1486.6 eV) and standard Mg/Al sources was used to determine the compositional information of the films. The Au 4f_{7/2} and Cu 2p_{3/2} excitations at 84.0 eV and 932.6 eV were used for energy calibration, and the atomic concentration was calculated by using the sensitivity factors provided with the PHI™ acquisition software. Analysis spot size can be varied from 1 × 0.8 mm\(^2\) to 0.4 × 0.4 mm\(^2\) with energy resolution of better than 0.5 eV. The base pressure for the analyzer system was less than 3 × 10\(^{-10}\) Torr. The films were subjected to an Ar\(^+\) ion bombardment using 4 kV Ar\(^+\) ions at 3 \(\mu\)A total target current to remove the surface oxide layer before the XPS analysis.

Figure 4.1. Neocera pulsed laser deposition system.
RESULTS AND DISCUSSION

PLD was chosen to fabricate AlMgB\textsubscript{14} films in this work because it is one of the most widely used physical vapor deposition (PVD) methods for depositing multicomponent thin films, with good capability of accurately preserving the target stoichiometry in the film due to congruent ablation induced by high-intensity laser irradiation of the target.\textsuperscript{29} The atomic concentrations of the constituents of as-deposited films are shown as a function of substrate temperatures in Table 4.2. It can be seen that the atomic ratio of Al, Mg and B for the film deposited at room temperature is very close to 1:1:14 stoichiometry with ~ 2.3 at.% Al in excess. The oxygen content (9.53 at.\%) is higher than expected in view of the vacuum level achieved (base pressure $\sim 8 \times 10^{-7}$ Torr), which may be due to the high affinity of Al and Mg for oxygen and low deposition rate caused by low laser energy (70 mJ). Low laser power was used to prevent particulate incorporation into the growing films. The oxygen partial pressure was measured using a residual gas analyzer (RGA) at a base pressure of $6 \times 10^{-7}$ Torr, and oxygen partial pressure was close to $1 \times 10^{-7}$ Torr. At $10^{-6}$ Torr partial pressure, the atomic flux of any gaseous species is about a monolayer per second, hence oxygen incorporation levels can be quite high in the films if the sticking coefficient of oxygen is relatively high. Baking out the chamber could reduce the oxygen content, but some degree of contamination in the films is unavoidable in light of the MgAl\textsubscript{2}O\textsubscript{4} content of the AlMgB\textsubscript{14} target. The Fe in the films arises from steel mill vial and media wear debris introduced into the target material during the high energy ball mill process used to produce the target.\textsuperscript{8} For the film deposited at 573 K, the Al, Mg, and B contents were found to deviate slightly from 1:1:14 stoichiometry with $\sim 2.3$ at.% excess Al, and $\sim 1.1$ at.% Mg deficiency. However, in contrast to the room temperature and 573 K-deposited films, the 873 K-deposited film
showed a marked increase of C content, jumping from ~ 2 at.% (the practical noise level for C in the XPS measurement) to 13 at.%. Meanwhile, the amount of Mg incorporation drops to only 2.08 at.%, a sharp decrease from the 4.98 at.% Mg of fully stoichiometric film deposited at room temperature. Since Mg has a high vapor pressure over a broad temperature range, one might expect the Mg content to decrease with rising substrate temperature.

### TABLE 4.2. Composition of as-deposited Al-Mg-B films

<table>
<thead>
<tr>
<th>Substrate temperature (K)</th>
<th>B (at.%)</th>
<th>Al (at.%)</th>
<th>Mg (at.%)</th>
<th>O (at.%)</th>
<th>Fe (at.%)</th>
<th>C (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>71.46</td>
<td>7.41</td>
<td>4.98</td>
<td>9.53</td>
<td>4.67</td>
<td>1.95</td>
</tr>
<tr>
<td>573</td>
<td>69.13</td>
<td>7.24</td>
<td>3.82</td>
<td>12.56</td>
<td>4.71</td>
<td>2.55</td>
</tr>
<tr>
<td>873</td>
<td>55.16</td>
<td>9.68</td>
<td>2.08</td>
<td>14.36</td>
<td>5.30</td>
<td>13.42</td>
</tr>
</tbody>
</table>

The six-fold increase in C content in the 873 K-deposited film is attributed to significant out-gassing and decomposition at 873 K of some C-containing molecules or volatile organic compounds adsorbed on the chamber wall and O-rings. Furthermore, a resputtering effect is believed to be another contributing factor, i.e., the growing film was sputtered somewhat by the highly energetic (~200-1000 kT) impinging species (mixed ions, atoms and molecules), leading to a dynamic balance between the deposition and sputtering processes. At the elevated substrate temperatures, the enhanced surface mobility of the C atoms promotes their reaction with Fe atoms to form carbide; thus, during deposition, the
resputtering effect on C atoms in the 873 K-deposited film is weaker than that in the room temperature and 573 K-deposited films, presumably because breaking the strong Fe-C bond in carbide formed in the film requires much higher energy than noncarbide forming films in which C atoms are loosely linked to the amorphous matrix. As a result, the 873 K-deposited film has much greater C content.

XPS compositional analysis was also performed on the films annealed at 1273 K. Although there is a negligibly small amount of Si present in the as-deposited films, the 1273 K-annealed films showed the presence of Si irrespective of substrate temperatures, and the Si concentration was found to decrease monotonically from about 9 at.% to 4.3 at.% as substrate temperatures increased (Figure 4.2). The presence of Si in the 1273 K-annealed films is not particularly surprising in a thin film with a SiO$_2$/Si substrate. The thermally activated migration of Si from the substrate and/or its oxide layer into the films during annealing at 1273 K indicates the failure of the amorphous SiO$_2$ layer as a diffusion barrier at this temperature. It is well known that substrate temperature plays an important role in determining thin film microstructure, therefore the effect of substrate temperatures on the Si concentration shown in Figure 4.2 can be attributed to different microstructures associated with different substrate temperatures. At low substrate temperatures, owing to limited surface mobility, there is not enough time for adatoms to find positions of energy minima before being constrained by subsequently deposited atoms, thus these atoms are “quenched” onto the substrate surface, facilitating the formation of non-equilibrium film structure with a high defect density. The various defects, such as vacancies, pinholes, and microporosity, etc., are believed to provide an effective pathway for faster Si outdiffusion. For the same deposition rate but higher substrate temperatures, reduced defect concentrations and denser
structures can be expected, hence effectively retarding Si migration into the films. Consequently, film deposited at a higher substrate temperature would be expected to contain less Si after annealing, as shown in Figure 4.2.

![Figure 4.2. Relation between Si concentration (at.%) in the 1273 K-annealed films and substrate temperatures during film deposition.](image-url)
Figure 4.3 (a) shows the XRD patterns for the room temperature as-deposited film, the room temperature-deposited 1173 K-annealed film and the room temperature-deposited 1273 K-annealed film. Aside from the Si (200) reflection centered at 2\(\theta\) ~ 33°, the XRD pattern for as-deposited film exhibits no diffraction features; this is indicative of an amorphous or nearly amorphous film structure. Although the Si (200) is a "forbidden" peak, it can appear because of growth-induced compressive stress leading to a slight distortion of the Si unit cell from cubic to tetragonal. The XRD pattern for the film annealed at 1173 K remains unchanged compared with the as-deposited film, suggesting that the amorphous structure persists up to 1173 K. Another possibility is that the film has a nanocrystalline structure with extremely fine grain size which can not be detected by XRD 0-2\(\theta\) scans. TEM-based structural investigations would be needed to further explore this issue. The XRD pattern for the 1273 K-annealed film shows four sharp diffraction peaks originating from the film, indicating that the film has been rendered fully crystalline at this annealing temperature. The peak centered at 2\(\theta\) = 17.27° can be ascribed to c-axis oriented tetragonal \(\alpha\)-FeSi\(_2\) phase. Three additional peaks centered at 2\(\theta\) positions of 13.85°, 27.89° and 42.37° were identified to correspond to (011), (022) and (033) planes of the AlMgB\(_{14}\) orthorhombic structure respectively; obviously, a strong (011) crystallographic texture has developed. It should be noted that the intensity ratio of the (022) peak to the (033) peak, \(I_{(022)}/I_{(033)}\), is approximately 1:3 and agrees well with the standard AlMgB\(_{14}\) powder diffraction pattern, whereas the intensity of the (011) peak relative to that of the (022) and (033) peaks appears to be abnormally faint, which is thought to be a consequence of the special low-angle diffraction geometry for a small, thin film sample.
The XRD patterns for the 573 K as-deposited film, the 573 K-deposited 1173 K-annealed film and the 573 K-deposited 1273 K-annealed film are presented in Figure 4.3 (b). The as-deposited film is apparently amorphous, and the film annealed at 1173 K is either amorphous or nanocrystalline. The XRD pattern for the 1273 K-annealed film explicitly shows the AlMgB14 orthorhombic structure with the (011) preferred orientation. The peak corresponding to α-FeSi2 phase is barely discernible, probably due to the fact that there is insufficient Si in the 573 K-deposited 1273 K-annealed film (Figure 4.2) to allow for formation of substantial amounts of α-FeSi2 phase. Therefore annealing the 573 K-deposited film at 1273 K yields predominantly single-phase AlMgB14.

As Table 4.2 shows, the room temperature and 573 K as-deposited films contained 9.53 at.% and 12.56 at.% O respectively, which has the potential to substantially alter the specimen composition and microstructure. The effect of O impurity has been studied in bulk AlMgB14.30 That study demonstrated that O prevents formation of single-phase AlMgB14. The O reacts with Al and Mg to form spinel MgAl2O4 phase, and if Fe impurity is present from milling wear debris, the O also reacts with Fe to form spinel Fe2O4 phase. Hence a three-phase structure of AlMgB14, Fe2O4, and MgAl2O4 typically forms in bulk material with O impurities. TEM analysis of such bulk material shows distinct spinel phases juxtaposed with pure AlMgB14 phases; no evidence of quaternary or higher order compounds was reported. Thus, it is a strong possibility that appreciable amounts of spinel phases also formed in the room temperature-deposited 1273 K-annealed film and the 573 K-deposited 1273 K-annealed film, although their volume percentages were apparently too low to produce discernible peaks in the XRD patterns.
Figure 4.3 (a) XRD patterns for the room temperature as-deposited film, the room temperature-deposited 1173 K-annealed film and the room temperature-deposited 1273 K-annealed film.
Figure 4.3 (Cont.) (b) XRD patterns for the 573 K as-deposited film, the 573 K-deposited 1173 K-annealed film and the 573 K-deposited 1273 K-annealed film.
The XRD patterns for the 873 K as-deposited film, the 873 K-deposited 1173 K-annealed film and the 873 K-deposited 1273 K-annealed film are shown in Figure 4.3 (c). Aside from the Si (200) reflection, no diffraction peaks can be observed in any of the three cases, demonstrating that the amorphous structure remains stable even by annealing at 1273 K. Because a significant amount of C impurity gets incorporated into the 873 K-deposited film, it seems likely that C plays a critical role in stabilizing the amorphous structure. In other studies, the presence of C impurity was reported to promote the formation of $\beta$-AlB$_{12}$.
phase in preference to AlMgB\textsubscript{14},\textsuperscript{21} thus it appears that the C content in films needs to be as low as possible in order to obtain the orthorhombic AlMgB\textsubscript{14} structure. It should be pointed out that the presence of a large amount of oxygen (14.36 at.\%) in the 873 K-deposited film might be able to further inhibit the formation of crystalline AlMgB\textsubscript{14} phase because the oxidation of Al, Mg and B was more energetically favorable, yielding a complex oxide glass structure with B playing the role of network former.\textsuperscript{31}

Strong crystallographic textures are commonly observed in polycrystalline thin films grown by PVD techniques. A variety of physical properties are influenced substantially by the film texture.\textsuperscript{32-34} Understanding how the texture develops in AlMgB\textsubscript{14} film, therefore, is necessary for achieving control of its microstructure and properties. The previous study by Higashi \textit{et al}\textsuperscript{35} showed that typical plate-like AlMgB\textsubscript{14} single crystals were bounded by well-developed (001) plane, indicating that the (001) plane may have the minimum surface energy. In principle, closest-packed planes with the minimum surface energy tend to be aligned parallel to the film surface (fiber texture), however, the XRD results in the present study clearly show the development of strong (011) texture rather than (001) texture in the 1273 K-annealed AlMgB\textsubscript{14} films. This phenomenon can be explained in terms of the following mechanism: based on the observation of a columnar grain structure by AFM (discussed later), the nucleation of a crystalline AlMgB\textsubscript{14} phase in an amorphous AlMgB\textsubscript{14} matrix is presumed to initiate at the substrate surface, the situation is quite similar to heterogeneous nucleation and growth of thin films from a vapor or liquid phase. It is common for vapor-deposited thin films to adopt an orientation that does not correspond with the lowest energy surface. For example, the \{110\} planes of bcc Cr have the lowest surface energy; however, Cr films grown on a substrate which favors three-dimensional (3D)
nucleation (poor wetting), adopt (002) texture so as to expose the \{110\} lowest energy facets, while Cr films that completely wet a substrate (2D nucleation) grow with \{110\} texture.\(^3\) In analogy with Cr films, the incoherent interface between a crystalline AlMgB\(_{14}\) nucleus and the underlying amorphous SiO\(_2\) layer promotes 3D nucleation and growth due to poor wetting, hence the (011) texture is preferred since this configuration exposes the lowest energy (001) facets, thereby minimizing the total interfacial energy in the film.

The (001) texture is beneficial to mechanical properties of AlMgB\(_{14}\) film because there are greater numbers of B\(_{12}\) icosahedra, and thus a greater number of B-B bonds in the B\(_{12}\) network parallel to the (001) plane (Figure 4.4), leading to a significantly enhanced hardness on that plane.\(^3\) Consequently, the prevalence of (001) texture in AlMgB\(_{14}\) films is thought to be highly desirable for application as hard coatings. According to the aforementioned mechanism for texture evolution, to form the (001) texture depends on selection of the appropriate substrate material (good substrate wettability). It is essential for the substrate to have the crystal structure and lattice parameters similar to AlMgB\(_{14}\) so that the (001) texture may develop as a result of 2D nucleation and growth. This texturing mechanism for AlMgB\(_{14}\) film suggests possible benefits from a double deposition: first deposit an "underlayer" of AlMgB\(_{14}\), which can then be crystallized by annealing to serve as a structural template, followed by a subsequent deposition and annealing of AlMgB\(_{14}\) film to establish a (001) texture in the exposed surface.
Figure 4.4. Icosahedral B₁₂ network parallel to the (001) plane of orthorhombic AlMgB₁₄.

Figure 4.5 shows AFM images of the surface morphologies of AlMgB₁₄ films deposited at room temperature before and after 1273 K-annealing. The room temperature-as-deposited film (Figure 4.5 a) displays a smooth surface profile dominated by domed features, the root mean square (r.m.s.) roughness over a scan area of 2 × 2 μm² is about 1.91 nm. For the 1273 K-annealed film (Figure 4.5 b), surface cracks were observed, particularly along the edges of the film, appearing as a mosaic pattern. The film shows a few particles on its surface, which is a typical characteristic of the PLD method. Additionally, the film has become discontinuous by breaking up into islands of irregular shape with lateral size ranging
from ~ 200 nm to 800 nm, it appears that these islands may correspond to a crystalline columnar structure. Such an interpretation is supported by the fact that strong texture has developed in the 1273 K-annealed AlMgB14 films. The r.m.s. roughness of the 1273 K-annealed film is 15.58 nm over a scan area of 2 \times 2 \mu m^2.

AFM images of AlMgB14 films deposited at 573 K before and after 1273 K-annealing are presented in Figure 4.6. The surface of the 573 K-as deposited film (Figure 4.6 a) shows typical amorphous features with r.m.s. roughness as low as 0.92 nm over a scan area of 2 \times 2 \mu m^2, this atomically flat surface is intimately related to the highly energetic incident species produced by laser ablation.\textsuperscript{37} The surface of the 1273 K-annealed film (Figure 4.6 b) exhibits sharp spikes, which are thought to be the result of oriented grains "pushing" out of the film during crystallization, the r.m.s. roughness is 2.05 nm over a scan area of 2 \times 2 \mu m^2; the whole film is continuous and free of cracks.

Surface cracking was found on the room temperature-deposited 1273 K-annealed AlMgB14 film. Because the thermal expansion coefficient of the Si substrate (~ 4 \times 10^{-6}/K) is much less than that of crystalline AlMgB14 film (~ 9 \times 10^{-6}/K),\textsuperscript{38} a significant tensile stress built up as the film was cooled from the annealing at 1273 K, which is believed to be responsible for the crack formation. This tensile stress can be estimated from the following formula for thermal stress calculation:\textsuperscript{28}

\[
\sigma_t = \frac{E_f (\alpha_s - \alpha_f) \Delta T}{1 - \nu_f} \tag{2}
\]

where \(\sigma_t\) is thermal stress of the film, \(E_f\), \(\nu_f\) and \(\alpha_f\) are Young's modulus, Poisson's ratio and thermal expansion coefficient of the film respectively, \(\alpha_s\) is thermal
expansion coefficient of the substrate; for crystalline AlMgB\textsubscript{14} film, $E_f$ is about 509 GPa and $\nu_f$ is 0.1,\textsuperscript{23} on cooling from 1273 K annealing temperature, the thermal stress would be 2.75 GPa. The compressive intrinsic stresses for the room temperature and 573 K as-deposited AlMgB\textsubscript{14} films were about 637 MPa and 278 MPa respectively, they were relaxed by annealing at 1273 K through thermally activated defects annihilation, therefore their contribution to the crack formation is negligible.

The 573 K-deposited 1273 K-annealed AlMgB\textsubscript{14} film, nevertheless, does not show any evidence of surface cracking, even though subjected to a large tensile stress. This phenomenon may be attributable to the different microstructures for the 1273 K-annealed films. The room temperature-deposited 1273 K-annealed AlMgB\textsubscript{14} film consists of two phases: orthorhombic AlMgB\textsubscript{14} phase and tetragonal $\alpha$-FeSi\textsubscript{2} phase, which differ in their thermal expansion coefficients ($\sim 6.7 \times 10^{-6}$/K for $\alpha$-FeSi\textsubscript{2}).\textsuperscript{39} During the cooling period of an annealing cycle, a high strain incompatibility arising from thermal expansion mismatch may develop at the phase boundaries in the presence of tensile stress, therefore the phase boundary becomes the site for crack initiation and provides an easy path for subsequent crack propagation, resulting in premature intergranular fracture of the film. By contrast, the 573 K-deposited 1273 K-annealed film is comprised of single-phase AlMgB\textsubscript{14}, hence it can withstand much greater tensile stress due to the absence of incompatible strain.
Figure 4.5. AFM images of (a) the room temperature-as deposited AlMgB_{14} film and (b) the room temperature-deposited, 1273 K-annealed AlMgB_{14} film.
Figure 4.6. AFM images of (a) the 573 K-as deposited AlMgB$_{14}$ film and (b) the 573 K-deposited, 1273 K-annealed AlMgB$_{14}$ film.
It is interesting to note that surface cracking was also found on the room temperature-deposited 1173 K-annealed AlMgB$_{14}$ film, which probably still retains amorphous structure according to the XRD pattern. However, if this is the case, it would be difficult to explain the origin of the high tensile stress responsible for the crack occurrence. Indeed, it seems plausible to assume that a nanocrystalline structure with extremely fine grain size might have formed, even though there is no direct experimental evidence.

Islands with holes in between exposing the substrate were developed in the room temperature-deposited 1273 K-annealed AlMgB$_{14}$ film, indicating that a microstructural instability has occurred. It is generally assumed that thin films will remain stable during processing and service; however, initially continuous films are not always thermodynamically stable and they can “dewet” or uncover the substrate during a high temperature heat treatment. This phenomenon, also termed “film agglomeration”, has been observed for a wide range of epitaxial and polycrystalline thin films. Film agglomeration proceeds with the nucleation and growth of holes driven by stress and capillarity effects, leading to an extremely porous, yet still contiguous film, as shown in Figure 4.5 (b). It has been recognized that defects play a critical role in holes formation, particularly grain boundary grooving. Film agglomeration is also very susceptible to the film thickness in that thinner films are prone to the formation of holes.

The observation of a microstructural instability only in the room temperature-deposited 1273 K-annealed AlMgB$_{14}$ film suggests that this phenomenon must be associated with its two-phase microstructure. As described above, during the 1273 K-annealing process, there is a variation in tensile stress from phase to phase due to the difference in thermal expansion coefficients and elastic moduli between orthorhombic AlMgB$_{14}$ phase and
tetragonal $\alpha$-FeSi$_2$ phase. A grain with a lower tensile stress will lose material to grains where the tensile stress is high, giving rise to the sinking or thinning of such grains and the formation of a hole in the film. Grain sinking was shown to be the major mechanism for holes formation in thick Al film when the film was in tension.\textsuperscript{41} Moreover, pre-existing holes greater than a critical size also will initiate film agglomeration,\textsuperscript{43} and deposition of AlMgB$_{14}$ film at room temperature inherently involves the formation of such holes due to its low density amorphous structure. Densification as well as holes growth and coalescence are concurrent during subsequent high temperature annealing, resulting in the eventual development of island-like surface morphology for the room temperature-deposited 1273 K-annealed AlMgB$_{14}$ film.

CONCLUSIONS

Al-Mg-B thin films were deposited on SiO$_2$/Si substrates by nanosecond PLD technique at different substrate temperatures, the post-deposition annealing was performed at 1173 K or 1273 K for two hours. The results of XPS, XRD and AFM show that the as-deposited films are amorphous, and annealing at 1173 K yields either amorphous or nanocrystalline structure. Significant formation of orthorhombic AlMgB$_{14}$ phase with strong (011) texture has occurred in the room temperature and 573 K-deposited Al-Mg-B films via annealing at 1273 K, a mechanism for (011) texture development is proposed based on minimization of interfacial free energy; however, the orthorhombic AlMgB$_{14}$ phase was not attained for the 873 K-deposited 1273 K-annealed films, which is thought to result from the high C content and non-stoichiometric composition in this film. The introduction of substantial amounts of Si into the room temperature-deposited 1273 K-annealed AlMgB$_{14}$
film from SiO$_2$/Si substrate leads to the coexistence of orthorhombic AlMgB$_{14}$ phase and tetragonal $\alpha$-FeSi$_2$ phase, which is thought to be responsible for the crack formation and microstructural instability observed in this film. The 573 K-deposited 1273 K-annealed AlMgB$_{14}$ film consists of single-phase orthorhombic AlMgB$_{14}$; this film is relatively smooth and free of cracks, which makes it the most suitable for mechanical and electrical characterization, such as nanoindentation, electrical conductivity measurement, etc. We plan to perform such tests in the near future on these films.

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REFERENCES


CHAPTER 5. SUPERHARD SELF-LUBRICATING AlMgB₁₄ FILMS FOR MICROELECTROMECHANICAL DEVICES


ABSTRACT

Performance and reliability of microelectromechanical system (MEMS) components can be enhanced dramatically through the incorporation of protective thin film coatings. Current-generation MEMS devices prepared by the Lithographie-Galvanoformung-Abformung (LIGA) technique employ transition metals such as Ni, Cu, Fe, or alloys thereof, and hence lack stability in oxidizing, corrosive, and/or high temperature environments. Fabrication of a superhard, self-lubricating coating based on a ternary boride compound AlMgB₁₄ is described in this letter as a potential breakthrough in protective coating technology for LIGA microdevices. Nanoindentation tests show that hardness of AlMgB₁₄ films prepared by pulsed laser deposition (PLD) ranges from 45 GPa to 51 GPa, when deposited at room temperature and 573 K, respectively. Extremely low friction coefficients of 0.04 – 0.05, which are thought to result from a self-lubricating effect, have also been confirmed by nanoscratch tests on the AlMgB₁₄ films. Transmission electron microscopy studies show that the as-deposited films are amorphous, regardless of substrate temperature; however, analysis of Fourier transform infrared spectra (FTIR) suggests that the higher substrate temperature facilitates formation of the B₁₂ icosahedral framework, therefore leading to the higher hardness.
INTRODUCTION

Microelectromechanical Systems (MEMS) are among the most significant technological advances of the last two decades. Bulk micromachining and surface micromachining have become primary processing techniques for fabrication of MEMS devices derived from Si and Si-based materials. However, there is a major drawback associated with the bulk and surface micromachining: low geometric aspect ratio, which severely limits their further applications. To meet the critical need for high-aspect-ratio microdevices, the Lithographie-Galvaniformung-Abformung (LIGA) technique, based on deep X-ray lithography and electroplating, has been developed and studied. The LIGA process is capable of producing microdevices a few centimeters high with an aspect ratio of more than 100, which is particularly advantageous for microdevices such as micromotors and micropumps since the high aspect ratios allow the generation of high torque. In addition, the LIGA process also allows one to use conventional materials such as metals for the MEMS architectures.

It is becoming increasingly important to fabricate LIGA microdevices capable of operating in harsh environments, such as high contact stresses (microgear sets), high temperatures (microcombustion chambers), and corrosive environments (microheat exchangers or microcatalytic converters). Nonetheless, most LIGA microdevices are manufactured out of Ni, Cu, Fe or their alloys, whose performance would be significantly degraded in these demanding situations, even to the extent of total failure. Recently, surface treatment by coatings has been recognized as an effective method to alleviate this serious problem and substantially prolong the lifetime of LIGA microdevices. The characteristics of an ideal protective coating for LIGA microdevices are: low wear rate, low coefficient of
friction, low thermal conductivity, strong adhesion, chemical inertness, and high temperature stability. Protective coatings with the potential to form a lubricating film on their surfaces (self-lubricating) are particularly desirable for reducing friction and wear in LIGA microdevices.\(^{10}\)

Diamond-like carbon (DLC) films have been explored for this use,\(^{11}\) however, a high compressive residual stress of several GPa usually develops in DLC films, causing delamination of films with thickness of greater than 100 nm. Moreover, DLC films are thermally unstable at temperatures above 723 K, which render them unsuitable for high temperature applications. Low-surface-energy, hydrophobic polymeric coatings are promising for minimizing stiction and friction,\(^{12}\) but they do not improve the wear resistance of LIGA microdevices because of their comparatively low hardness, and they fail at temperatures only moderately higher than ambient.

In this letter, we report fabrication of a new superhard AlMgB\(_4\) film, which could serve as an excellent protective coating for LIGA microdevices, or possibly Si-based MEMS components, due to its extremely high hardness, exceptionally low coefficient of friction (provided by self-lubricant), and strong adhesion to a wide range of substrate materials.\(^{13,14}\)

**EXPERIMENTAL PROCEDURE**

AlMgB\(_4\) films were prepared on Si (100) and carbon-coated copper grids using pulsed laser deposition (PLD) at room temperature and 573 K. The base pressure was maintained below 8 \(\times\) 10\(^{-7}\) Torr. Hot-pressed Al\(_{0.95}\)Si\(_{0.05}\)MgB\(_4\) was used as the target; synthesis of Al\(_{0.95}\)Si\(_{0.05}\)MgB\(_4\) was described in a previous publication.\(^{15}\) The microstructure of AlMgB\(_4\) films deposited on carbon-coated copper grids was examined directly with a
Philips CM30 transmission electron microscope (TEM) operated at 300 kV. A Bruker IFS 66v/S Fourier transform infrared (FTIR) spectrometer was employed to extract local bonding information. Surface roughness of the films was measured by a Digital Instruments Dimension 3100 atomic force microscope (AFM), the root mean square roughness was obtained over a scanning area of $0.3 \times 0.3 \, \mu\text{m}^2$. Nanoindentation with Hysitron TriboIndenter and a diamond cube corner tip (radius < 100 nm) was performed on the films to obtain the hardness and elastic moduli of the films as a function of the indentation depth, and the coefficient of friction was determined by a nanoscratch method with a conical diamond tip (radius = 1 \, \mu\text{m}), the sliding speed was set at 133 nm/s under a load of 10-100 \mu\text{N}, the sliding distance was 4 \, \mu\text{m}.

In nanoindentation test, the load was gradually increased to a pre-set maximum value such that both elastic and plastic deformation occurred in the film. The load was then released, causing partial or complete relaxation. The unloading was dominated by elastic displacements. Nanohardness and modulus were obtained from the load-displacement curves based on the improved method\cite{16}. First, the contact stiffness $S$ and the contact depth $h_c$ were determined from load-displacement curves. Second the hardness $H$ and the modulus $E$ were calculated from the following equations:

\begin{equation}
H = \frac{P_{\text{max}}}{A_c} \quad \text{and} \quad \frac{1-v_i^2}{E_i} + \frac{1-v^2}{E} = \frac{2}{\sqrt{\pi}} \frac{\sqrt{A_c}}{S}
\end{equation}

where $A_c$ is the projected contact area obtained from the contact depth, $E_i$ and $v_i$ are the modulus and Poisson’s ratio of the indenter respectively, $E$ and $v$ are the modulus and Poisson’s ratio of the tested sample.
RESULTS AND DISCUSSION

Figure 5.1 shows a plan-view bright field TEM image of AlMgB\textsubscript{14} film deposited at 573 K. The selected area diffraction pattern (SADP) from this film is presented in the inset, in which a halo (diffuse) rings pattern is clearly evident. Furthermore, static and conical dark field images do not show any nanocrystalline structure, indicating that the film is primarily amorphous. Small particles are occasionally observed in the film. It is rather interesting to note that the film exhibits a maze pattern; an energy dispersive spectroscopy (EDS) study showed a homogeneous film composition across the bright and dark stripes. It was therefore speculated that the observed maze pattern might be caused by variation in film thickness, which is believed to be a consequence of non-uniform contraction of the AlMgB\textsubscript{14} film upon cooling from 573 K due to thermal expansion mismatch between the Cu grid and amorphous AlMgB\textsubscript{14} film. The TEM image and SADP of AlMgB\textsubscript{14} film deposited at room temperature are similar to those of 573 K-deposited AlMgB\textsubscript{14} film indicative of the amorphous structure in this film, except that the former does not show any maze pattern.

Figure 5.2 shows the FTIR spectra of AlMgB\textsubscript{14} films deposited at the two different substrate temperatures. For the room temperature-deposited AlMgB\textsubscript{14} film, it can be seen that there is a weak absorption in the vicinity of 1000 cm\textsuperscript{-1}, which could be assigned to an overlapping of $A_{2u}$ and $E_u$ vibrational modes of a single B\textsubscript{12} icosahedron\textsuperscript{17}. The low absorption intensity indicates that the B\textsubscript{12} icosahedron was not fully developed at this deposition temperature. For the AlMgB\textsubscript{14} film deposited at 573 K, however, a stronger absorption is observed at $\sim$ 1100 cm\textsuperscript{-1}, which can be ascribed to the $F_{1u}$ vibrational mode of a single B\textsubscript{12} icosahedron\textsuperscript{18}. This is a breathing mode characterized by two half-icosahedra
vibrating against each other. The strong absorption intensity suggests that well-formed B_{12} icosahedra are present in the 573 K-deposited AlMgB_{14} film.

Figure 5.1. Bright field TEM image of the 573 K-deposited AlMgB_{14} film (plan view). The inset is the selected area diffraction pattern.

Figure 5.3 shows the AFM images of AlMgB_{14} films deposited at room temperature and 573 K. This figure illustrates that very smooth AlMgB_{14} films have been produced by the PLD technique, although some particulates, an artifact of the PLD process, are incorporated into the films. The surface roughnesses are 0.736 nm and 0.171 nm for the
room temperature and 573 K-deposited AlMgB₁₄ films respectively. The decrease in surface roughness at higher substrate temperature may be due to an enhanced surface mobility of adatoms, hence increasing the areal density of nucleation sites and reducing surface roughness.

Figure 5.2. FTIR spectra of the room temperature and 573 K-deposited AlMgB₁₄ films.
Figure 5.3. AFM images (0.3 $\times$ 0.3 $\mu m^2$) of (a) the room temperature-deposited AlMgB$_{14}$ film and (b) the 573 K-deposited AlMgB$_{14}$ film.
The measured hardness and moduli of the room temperature and 573 K-deposited AlMgB$_{14}$ films are plotted in Figure 5.4, as a function of indentation contact depth. Both hardness and modulus decrease and approach those of the substrate (Si) with increasing indentation contact depth, exhibiting typical behavior of a hard film on a soft substrate.\textsuperscript{19} If the film is harder than the substrate, then most of the plastic deformation would occur within the softer substrate, leading to a “sink-in” effect even if the indenter had not yet penetrated through the film.\textsuperscript{19} Since the influence of the substrate rises as the indentation depth increases, in order to determine the hardness of the film alone, a widely accepted rule of thumb calls for limiting the indentation depth to less than 10\% to 15\% of the film thickness. Figure 5.4 shows that the maximum hardness for the room temperature and 573 K-deposited AlMgB$_{14}$ films are 45 GPa and 51 GPa respectively; these values correspond to an indentation depth of less than 10\% of the film thickness (~ 300 nm to 400 nm), indicating that these hardness values may be very close to the true hardness of AlMgB$_{14}$ films.

Extraordinarily high hardness has been reported in superlattices and nanocomposite coatings, where interfacial phenomena govern the mechanical properties. Veprek \textit{et al.} refer to such a microstructural contribution to hardness as “extrinsic hardness”.\textsuperscript{20} In this work, superhardness of 45 GPa and 51 GPa was achieved for the room temperature and 573 K-deposited AlMgB$_{14}$ films; however, it should be noted that such high hardness was essentially obtained in an entirely amorphous structure, in which randomly distributed B$_{12}$ icosahedra dominate according to the FTIR results. This appears to indicate that AlMgB$_{14}$ films derive their extreme hardness from the covalent, intraicosahedral B-B bonds, and the hardening mechanism for AlMgB$_{14}$ films should be considered as “intrinsic”, which is the case for conventional superhard materials, such as diamond and c-BN. The higher hardness
(51 GPa) for the AlMgB$_{14}$ film deposited at 573 K may be due to its denser structure and formation of more well-developed B$_{12}$ icosahedra at higher deposition temperatures, as indicated by the FTIR spectra.

Figure 5.4 (a) Hardness versus indentation contact depth for AlMgB$_{14}$ films on Si substrates. The inset is the AFM image of indentation. The hardness data of substrates were collected from a region of the substrates masked during deposition which consequently lacked any AlMgB$_{14}$ film.
Figure 5.4 (Cont.) (b) Reduced moduli ($E_r$) versus indentation contact depth for AlMgB$_{14}$ films on Si substrates. The inset is the AFM image of indentation. The moduli data of substrates for 300 K deposition (○) and 573 K deposition (◇) were collected from a region of the substrates masked during deposition which consequently lacked any AlMgB$_{14}$ film.
What is scientifically intriguing about AlMgB\textsubscript{14} films is that the B-B bonding in B\textsubscript{12} icosahedra is indeed electron deficient,\textsuperscript{21} consequently the hardness is expected to be much lower than that of conventional superhard materials,\textsuperscript{22} whose crystal structures are typically based upon highly directional, covalent sp\textsuperscript{3} bonds. In this work, however, a hardness comparable to that of c-BN has been obtained in AlMgB\textsubscript{14} films. This anomaly might be associated with the incorporation of metallic dopants (i.e. Al and Mg) in AlMgB\textsubscript{14} films. It has been shown by electron density mapping that a substantial number of valence electrons can transfer from metal atoms to the boron framework in the AlMgB\textsubscript{14}-type orthorhombic borides,\textsuperscript{23} leading to a full occupancy of valence band of B\textsubscript{12} icosahedra\textsuperscript{24} and thus, much stronger B-B bonds. This effect could be further enhanced in amorphous structures.

The friction coefficients of the room temperature and 573 K-deposited AlMgB\textsubscript{14} films were found to be extremely low, ranging between 0.04 and 0.05. Such low friction behavior can be attributed to the \textit{in situ} formation of a very lubricious surface layer of boric acid (H\textsubscript{3}BO\textsubscript{3}), which acts as a self-lubricant for AlMgB\textsubscript{14} films. Boric acid is an end product of sequential reactions among B, O and H\textsubscript{2}O in the air,\textsuperscript{25} it is characterized by a layered triclinic crystal structure similar to that of graphite, MoS\textsubscript{2}, and h-BN, i.e., closely packed H, B and O atoms in each layer are strongly linked to each other by covalent and ionic bonds, whereas weak van der Waals forces prevail between the atomic layers (Figure 5.5). Hence, when in sliding contact with another solid surface, adjacent atomic layers in boric acid can be easily shear-deformed, which results in a low friction coefficient. Such layered compounds have also been found on the surfaces of B\textsubscript{4}C and borided steel.\textsuperscript{25,26}
CONCLUSIONS

In summary, we have demonstrated growth of a superhard, atomically smooth, and self-lubricating AlMgB$_{14}$ film by pulsed laser deposition. Remarkable hardness of greater than 40 GPa was obtained from an entirely amorphous structure, this phenomenon can be accounted for based on an electron transfer mechanism from metal atoms present in the film. In particular, AlMgB$_{14}$ film is a very promising candidate for protective coating on LIGA microdevices and Si-based MEMS components. Although thin films of B$_{4}$C and boron suboxide (B$_{x}$O, x > 1) have been studied for possible hard coating applications, we believe this work is the first to examine use of AlMgB$_{14}$ films for such purpose.
ACKNOWLEDGEMENTS

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REFERENCES


CHAPTER 6. ELECTRICAL TRANSPORT IN AMORPHOUS SEMI-CONDUCTING 

AlMgB₁₄ FILMS

A paper submitted to Applied Physics Letters


ABSTRACT

The electrical transport properties of semi-conducting AlMgB₁₄ films grown at room temperature and 573 K are reported in this letter. As-deposited films are amorphous, and they exhibit high electrical conductivity originating from n-type carriers, which are believed to stem from the conduction electrons donated by Al, Mg and/or Fe impurity in these films. At the higher deposition temperature, AlMgB₁₄ films become less conductive due to a reduction in carrier concentration. This phenomenon may result from the nature of trap states in the band gap related to the different deposition temperatures.

INTRODUCTION

Boron-rich boride films are refractory semiconductors, which have been the subject of intense investigation in recent years due to their desirable properties,¹⁻⁵ including high hardness (> 30 GPa), high melting point (> 2000°C), low density, extremely low γ-radiation absorption, chemical inertness and thermal stability at high temperatures. These materials may be useful in electronic devices operating in a wide variety of extreme or harsh environments (mechanically abrasive, radiative, corrosive and/or high temperature). Successful implementation of these materials will require a thorough understanding of their electrical properties, which are profoundly influenced by their composition,⁶⁻⁷
microstructure and deposition methods. Considerable research on boron-rich boride films has focused on boron compounds with C, N, and O, such as $B_4C/B_5C$, $B_xN$ ($x > 1$) and boron suboxide ($B_xO$, $x > 1$) in terms of the electrical transport mechanism, dielectric properties, doping behavior, and device performance. Recently, the ternary boride compound $AlMgB_{14}$ has attracted attention due to its novel mechanical properties; however, no studies have been reported on its electrical properties in thin film form. This letter discusses the effect of microstructure on the electrical properties of $AlMgB_{14}$ films. Moreover, this study shows that $AlMgB_{14}$ films are unusual in two regards when compared to other boron-rich boride films: they are characterized by an unusually low resistivity, and the charge carriers are predominantly n-type, which are vital for the development of boron-rich boride-based semiconductor devices.

**EXPERIMENTAL PROCEDURE**

Pulsed laser deposition (PLD) was used for the growth of $AlMgB_{14}$ films on thermally oxidized Si (100) and 7059 glass at room temperature and 573 K respectively. The base pressure was maintained below $6 \times 10^{-7}$ Torr. Hot-pressed $Al_{0.95}Si_{0.05}MgB_{14}$ was used as the target; synthesis of this compound is described in a previous publication. The composition of $AlMgB_{14}$ films was determined by x-ray photoelectron spectroscopy (XPS). The electrical resistivity of $AlMgB_{14}$ films was measured at room temperature using the four-point probe and van der Pauw method. In addition, van der Pauw Hall measurements were carried out on $AlMgB_{14}$ films to determine the carrier type, carrier concentration and Hall mobility. The contacts were formed with Ag paint, and exhibited ohmic characteristics after 5 hour-baking at 100°C, as indicated by room temperature $I-V$ measurements performed on the films. A
hot probe method was also employed to determine the carrier type in AlMgB\textsubscript{14} films. The current under a constant voltage (fixed at 5 V) was recorded as a function of temperature from 300 K to 453 K, with Al stripes made by thermal evaporation as contacts. The films grown on 7059 glass were used for optical absorption measurements by a Perkin-Elmer UV-VIS-NIR spectrophotometer; the optical band gaps were determined by fitting the optical absorption spectra to the Tauc equation.

RESULTS AND DISCUSSION

PLD is considered a viable means of transferring target stoichiometry to the films, and this has been confirmed by XPS in the case of AlMgB\textsubscript{14} films (Table 6.1). XPS also indicated that there is no appreciable difference in composition between room temperature and 573 K-deposited AlMgB\textsubscript{14} films. The microstructure of AlMgB\textsubscript{14} films, which has been examined by transmission electron microscopy (Figure 5.1), remains amorphous regardless of substrate temperature.

<table>
<thead>
<tr>
<th>Deposition temperature</th>
<th>B (at.%)</th>
<th>Al (at.%)</th>
<th>Mg (at.%)</th>
<th>O (at.%)</th>
<th>C (at.%)</th>
<th>Si (at.%)</th>
<th>Fe (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>76.76</td>
<td>7.64</td>
<td>4.12</td>
<td>8.20</td>
<td>1.26</td>
<td>0.97</td>
<td>1.05</td>
</tr>
<tr>
<td>573 K</td>
<td>75.84</td>
<td>7.47</td>
<td>4.59</td>
<td>8.77</td>
<td>1.39</td>
<td>0.69</td>
<td>1.25</td>
</tr>
</tbody>
</table>
The electrical properties of AlMgB$_{14}$ films are presented in Table 6.2. Compared with the electrical resistivity of other boron-rich boride films, which cover a wide range of values from $\sim 10^3$ to $10^9$ $\Omega$cm, the electrical resistivity of room temperature and 573 K-deposited AlMgB$_{14}$ films is approximately three to eight orders of magnitude lower, approaching that of single crystal boron carbide.$^{10}$ It should be pointed out that such low resistivity was achieved in an entirely amorphous structure. Furthermore, the charge carriers in these AlMgB$_{14}$ films are dominated by electrons, as opposed to the p-type carriers (holes) which prevail in most boron-rich boride materials.

**TABLE 6.2. The electrical properties of as-deposited AlMgB$_{14}$ films (Si doped)**

<table>
<thead>
<tr>
<th>Deposition temperature</th>
<th>Resistivity ((\Omega)-cm)</th>
<th>Carrier type</th>
<th>Carrier concentration ((\text{cm}^{-3}))</th>
<th>Carrier mobility ((\text{cm}^2/\text{Vs}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>4.4 (4.5)</td>
<td>n</td>
<td>$2.85 \times 10^{17}$</td>
<td>4.86</td>
</tr>
<tr>
<td>573 K</td>
<td>38.2 (41.1)</td>
<td>n</td>
<td>$2.06 \times 10^{16}$</td>
<td>6.89</td>
</tr>
</tbody>
</table>

The low electrical resistivity observed in AlMgB$_{14}$ films is a consequence of a high carrier concentration combined with moderate carrier mobility. In general, the electrical phenomena common to all boron-rich boride materials, e.g., the electronic structure in particular, is essentially determined by the B$_{12}$ icosahedra. Figure 2.6 illustrates the electronic structure of $\beta$-rhombohedral boron,$^{13}$ which is typical for all the boron-rich boride materials. The valence band consists of an upper split-off subband VB$_1$, which is generated
by the Jahn-Teller distortions of the $B_{12}$ icosahedra, and a lower subband $VB_2$. $VB_1$ is partially occupied by electrons in low-density localized states; these electrons are thermally excited from $VB_2$ with free holes left behind, thus $VB_1$ acts like an intrinsic acceptor level in nature. Accordingly, two transport mechanisms are operative: electron hopping at the Fermi level in $VB_1$ and free hole conduction in the extended states of $VB_2$.\textsuperscript{13} Moreover, strong electron-phonon coupling in $B_{12}$ icosahedra leads to the formation of six intrinsic high-density trap levels in the band gap,\textsuperscript{14} as shown in Figure 2.6. For most boron-rich boride materials, electrical transport by holes predominates because the excited electrons can be easily captured in the trap states. Nevertheless, Lewis \textit{et al.} reported an extremely high n-type carrier concentration (~ $10^{21}$ cm$^{-3}$) and low carrier mobility (~ 0.133 cm$^2$/Vs) associated with hot-pressed $\text{AlMgB}_{14}$,\textsuperscript{15} which they attributed to electron hopping mechanism.

Neither electron hopping mechanism nor band-type conduction by holes can reasonably explain the unique electrical transport behavior of $\text{AlMgB}_{14}$ films. The significantly enhanced n-type carrier mobility observed in $\text{AlMgB}_{14}$ films (4.86 cm$^2$/Vs and 6.89 cm$^2$/Vs) suggests that it is the electrons, which are excited beyond the mobility edge into extended states of the conduction band,\textsuperscript{16} that play a major role in the electrical transport process of $\text{AlMgB}_{14}$ films. Moreover, the high carrier concentration ($2.85 \times 10^{17}$ cm$^{-3}$ and $2.06 \times 10^{16}$ cm$^{-3}$) indicates that these electrons are provided by metallic constituents (i.e., Al, Mg and/or Fe impurity) in $\text{AlMgB}_{14}$ films, because pure boron films typically have far lower p-type carrier concentrations (~ $10^{13}$ cm$^{-3}$).\textsuperscript{17} There are two pathways of introducing dopants into the boron-rich boride materials: substitution and network modification, with the latter one usually observed for metallic dopants like Fe and Ni in boron carbide.\textsuperscript{10} By network modification, metallic dopants simply fill the voids or interstitial positions in $B_{12}$ icosahedral
network and contribute their valence electrons to $B_{12}$ icosahedra through charge transfer. The
Al and Mg in AlMgB$_{14}$ films probably follow a similar mechanism as well. Fe impurity may
also be a donor in these films, just as it does in boron carbide and $\beta$-rhombohedral boron.
Figure 6.1 shows the plot of $\ln I$ versus $1/T$ for AlMgB$_{14}$ films indicating a perfect linear
relationship. It is somewhat unusual for amorphous semiconductors with complex
composition to exhibit such a "clean" doping behavior, i.e., only a single donor level is
activated to provide electrons. The activation energy for electrical conductivity, which can
be obtained from the slope of such a plot, is 0.13 eV for the room temperature-deposited
AlMgB$_{14}$ film and 0.17 eV for the 573 K-deposited AlMgB$_{14}$ film, indicating that the Al, Mg
and/or Fe in AlMgB$_{14}$ films may introduce a shallow donor level below the conduction band
edge. Due to the presence of Si (Table 6.1) in these films, the likelihood for Si being a donor
cannot be ruled out. Figure 6.2 presents the plot of $\ln I$ versus $1/T$ for baseline AlMgB$_{14}$
films (without Si), the activation energy is 0.11 eV for the room temperature-deposited film
and 0.19 eV for the 573 K-deposited film, suggesting that Si, however, does not have any
impact on electrical transport properties of AlMgB$_{14}$ film.

Transformation of p-type boron-rich boride materials to n-type by doping is not a
trivial task because of the difficulty in overcompensating the high-density trap states in the
band gap; an extremely high donor concentration on the order of $10^{20}$ cm$^{-3}$ is generally
required to enable this transformation.$^{18}$ In this study, however, n-type carriers can be
obtained in AlMgB$_{14}$ films by much lower donor concentrations. This is probably because
the six intrinsic trap states, which basically depend on the vibrational modes of $B_{12}$
icosahedra,$^{14}$ were not fully developed at the low deposition temperatures. Figure 6.3 shows
the Tauc plots of AlMgB$_{14}$ films, from which the optical band gaps are determined to be ~
0.5 eV, and it appears that deposition temperature does not have a strong effect on the optical band gaps. Therefore, the different carrier concentrations in AlMgB$_{14}$ films can only be attributed to the trap states of different characters, i.e., an increase in deposition temperature leads to a higher density of well-formed B$_{12}$ icosahedra,\textsuperscript{12} which, in turn, gives rise to more electron trapping states in the band gap. As the density of trap states increases, a decrease in carrier concentration is expected, which is what was observed in this study.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6a.png}
\caption{(a) Plot of $\ln I$ versus $1/T$ for the room temperature-deposited AlMgB$_{14}$ film (Si doped).}
\end{figure}
Figure 6.1 (Cont.) (b) Plot of ln I versus 1/T for the 573 K-deposited AlMgB\textsubscript{14} film (Si doped).

Figure 6.2 (a) Plot of ln I versus 1/T for the room temperature-deposited baseline AlMgB\textsubscript{14} film.
Figure 6.2 (Cont.) (b) Plot of $\ln I$ versus $1/T$ for the 573 K-deposited baseline AlMgB$_{14}$ film.

Figure 6.3 (a) Tauc plot of the room temperature-deposited AlMgB$_{14}$ film (Si doped).
CONCLUSIONS

In summary, amorphous semi-conducting AlMgB₁₄ films produced by PLD show an unusually low resistivity. High n-type carrier mobility demonstrates that the electrical transport behavior of AlMgB₁₄ films is mainly due to the band-type conduction by electrons, which are contributed by Al, Mg and/or Fe impurity serving as electron donors in AlMgB₁₄ films. The electrical properties of AlMgB₁₄ films are affected by deposition temperatures in such a manner that higher deposition temperatures tend to favor development of trap states in the band gap, hence resulting in a lower carrier concentration in the films.
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CHAPTER 7. CONCLUSIONS AND FUTURE WORK

In this work, baseline and doped AlMgB\textsubscript{14} thin film coatings have been synthesized by pulsed laser deposition (PLD) and investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), atomic force microscopy (AFM) and Fourier transform infrared (FTIR) spectrometry; the mechanical, electrical, and optical properties of AlMgB\textsubscript{14} thin films have been characterized by nanoindentation, four-point probe, van der Pauw Hall measurement, activation energy measurement, and UV-VIS-NIR spectrophotometer. It was found that a high vacuum level during the depositions is essential to produce good quality AlMgB\textsubscript{14} films. Appreciable amounts of contamination due to oxygen and carbon have been identified in AlMgB\textsubscript{14} films deposited under low vacuum levels; subsequent high temperature-annealing crystallized them, producing phases which did not coincide with the orthorhombic AlMgB\textsubscript{14} crystal structure. Nanohardness obtained from these films is mediocre (10 GPa).

Deposition of AlMgB\textsubscript{14} films using a new PLD system with substantially improved vacuum level yielded high quality AlMgB\textsubscript{14} films with nanohardness as high as 50 GPa even for an entirely amorphous structure. The substrate temperatures employed during deposition were found to affect the nanomechanical behaviors of AlMgB\textsubscript{14} films in such a manner that the higher substrate temperatures give rise to higher film hardness. Orthorhombic AlMgB\textsubscript{14} phase can be obtained by high temperature-annealing of such AlMgB\textsubscript{14} films accompanied by strong texture formation.

In addition to the excellent mechanical properties, these semi-conducting AlMgB\textsubscript{14} films also exhibit high n-type electrical conductivity. Al, Mg and/or Fe impurities are thought to serve as the active electron donors via charge transfer between these metallic
dopants and the $B_{12}$ icosahedral framework. The same mechanism has been proposed to account for the novel mechanical properties observed in these films as well. The combination of high hardness, good electrical conductivity, and low friction coefficient in these AlMgB$_{14}$ thin film coatings make them potentially useful for a variety of applications.

Future research work will explore the thin film deposition by ablation of a TiB$_2$ doped-AlMgB$_{14}$ PLD target. Such deposition could produce a nanocomposite microstructure: nanoscaled TiB$_2$ crystallites embedded in the amorphous AlMgB$_{14}$ matrix, and such a structure would be expected to display both higher hardness and greater electrical conductivity. Deposition of AlMgB$_{14}$ thin film coatings by higher deposition rate PVD methods (e.g., DC/RF magnetron sputtering, vacuum arc deposition, etc.) would also be worth developing.
APPENDIX. X-RAY PHOTOELECTRON SPECTROSCOPY

Surface analysis by X-ray photoelectron spectroscopy (XPS) is accomplished by irradiating a sample with monoenergetic soft X-rays and analyzing the energy of the detected electrons. Mg Kα (1253.6 eV) or Al Kα (1486.6 eV) X-rays are usually used. These photons have limited penetrating power in a solid on the order of 1-10 micrometers. They interact with atoms in the surface region, causing electrons to be emitted by the photoelectric effect. The emitted electrons have measured kinetic energies given by:

\[ KE = h\nu - BE - \Phi_s \]  \hspace{1cm} (1)

where \( h\nu \) is the energy of the photon, \( BE \) is the binding energy of the atomic orbital from which the electron originates, and \( \Phi_s \) is the spectrometer work function.

The binding energy may be regarded as the energy difference between the initial and final states after the photoelectron has left the atom. Because there is a variety of possible final states of the ions from each type of atom, there is a corresponding variety of kinetic energies of the emitted electrons. Moreover, there is a different probability or cross-section for each final state. Because each element has a unique set of binding energies, XPS can be used to identify and determine the concentration of the elements in the surface. Variations in the elemental binding energies (the chemical shifts) arise from differences in the chemical potential and polarizability of compounds. These chemical shifts can be used to identify the chemical state of the materials being analyzed.

Probabilities of electron interaction with matter far exceed those of the photons, so while the path length of the photons is of the order of micrometers, that of the electrons is of the order of tens of Ångstroms. Thus, while ionization occurs to a depth of a few
micrometers, only those electrons that originate within tens of Ångstroms below the solid surface can leave the surface without energy loss. Those electrons which leave the surface without energy loss produce the peaks in the spectra and are the most useful.

For many XPS investigations, it is important to determine the relative concentrations of the various constituents. Methods have been developed for quantifying the XPS measurement utilizing peak area and peak height sensitivity factors. The approach which utilizes peak area sensitivity factors typically is the more accurate and is satisfactory for quantitative work. For a sample that is homogeneous in the analysis volume, the number of photoelectrons per second in a specific spectra peak is given by:

\[ I = n f o \sigma \theta y \lambda A T \]  

(2)

where \( n \) is the number of atoms of the element per \( \text{cm}^3 \) of the sample, \( f \) is the X-ray flux in photons/cm\(^2\)-sec, \( \sigma \) is the photoelectric cross-section for the atomic orbital of interest in cm\(^2\), \( \theta \) is an angular efficiency factor for the instrumental arrangement based on the angle between the photon path and detected electron, \( y \) is the efficiency in the photoelectric process for formation of photoelectrons of the normal photoelectron energy, \( \lambda \) is the mean free path of the photoelectrons in the sample, \( A \) is the area of the sample from which photoelectrons are detected, and \( T \) is the detection efficiency for electrons emitted from the sample. From Equation (2):

\[ n = I / (f o \sigma \theta y \lambda A T) \]  

(3)

The denominator in Equation (2) can be defined as the atomic sensitivity factor, \( S \). If we consider a strong line from each of two elements, then

\[ \frac{n_1}{n_2} = \frac{I_1/S_1}{I_2/S_2} \]  

(4)
This expression may be used for all homogeneous samples if the ratio $S_1/S_2$ is matrix-independent for all materials. It is certainly true that such quantities as $\sigma$ and $\lambda$ vary somewhat from material to material (especially $\lambda$), but the ratio of each of the two quantities $\sigma_1/\sigma_2$ and $\lambda_1/\lambda_2$ remains nearly constant. Thus, for any spectrometer, it is possible to develop a set of relative values of $S$ for all of the elements. Multiple sets of values may be necessary for instruments with multiple X-ray sources at different angles relative to the analyzer.

A general expression for determining the atom fraction of any constituent in a sample, $C_x$, can be written as an extension of Equation 7:

$$C_x = \frac{n_x}{\sum n_i} = \frac{I_x/S_x}{\sum I_i/S_i}$$  \hspace{1cm} (5)
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