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Superhard self-lubricating AlMgB₁₄ films for microelectromechanical devices

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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 described in this letter has great potential in protective coating technology for LIGA microdevices. Nanoindentation tests show that the hardness of AlMgB₁₄ films prepared by pulsed laser deposition 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 suggests that the higher substrate temperature facilitates the formation of the B₁₂ icosahedral framework, therefore leading to the higher hardness.

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Microelectromechanical systems (MEMS) are among the most significant technological advances of the last two decades. To meet the critical need for high-aspect-ratio microdevices, the lithographie-galvanoformung-abformung (LIGA) technique, based on deep x-ray lithography and electroplating, has been developed and studied.^{1,2} The LIGA process allows use of 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.^{3–5} 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.⁶

Diamondlike carbon (DLC) films have been explored for this use,⁷ however, a high compressive residual stress of several GPa usually develops in DLC films, causing delamination of films with a 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,⁸ 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 the fabrication of a superhard AlMgB₁₄ 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),

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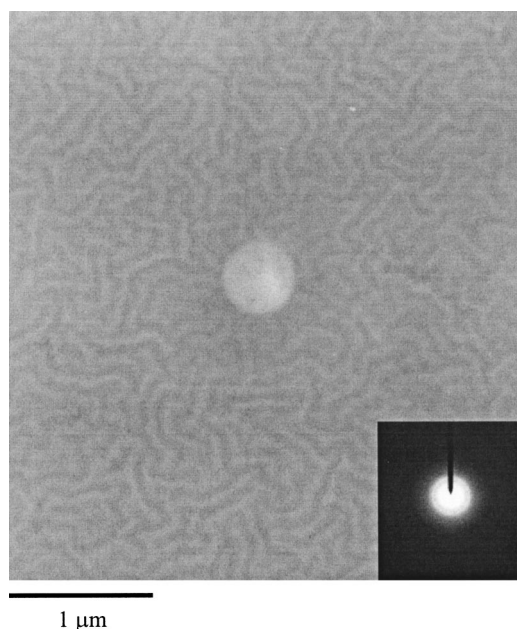


FIG. 1. Bright-field TEM image of the 573 K-deposited AlMgB₁₄ film (plan view). The inset is the SADP.

and strong adhesion to a wide range of substrate materials.^{9,10}

AlMgB₁₄ 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 8×10^{-7} Torr. Hot-pressed Al_{0.95}Si_{0.05}MgB₁₄ was used as the target; synthesis of Al_{0.95}Si_{0.05}MgB₁₄ was described in a previous publication.¹¹ The microstructure of AlMgB₁₄ 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. Nanoindentation with a 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 μm), the sliding speed was set at 133 nm/s under a load of 10–100 μN, the sliding distance was 4 μm.

Figure 1 shows a plan-view bright-field TEM image of AlMgB₁₄ film deposited at 573 K. The selected area diffraction pattern (SADP) from this film is presented in the inset, in which a halo (diffuse) ring pattern is clearly evident. Furthermore, static and conical dark-field images do not show any nanocrystalline structure, indicating that the film is primarily amorphous. It is rather interesting to note that the film exhibits a maze pattern; an energy dispersive spectroscopy 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 a variation in film thickness, which is believed to be a consequence of nonuniform contraction of the AlMgB₁₄ film upon cooling from 573 K due to the thermal expansion mismatch between the Cu grid and amorphous AlMgB₁₄ film. The TEM image and SADP of the AlMgB₁₄ film deposited at room temperature are similar to those of 573 K-deposited AlMgB₁₄ film except

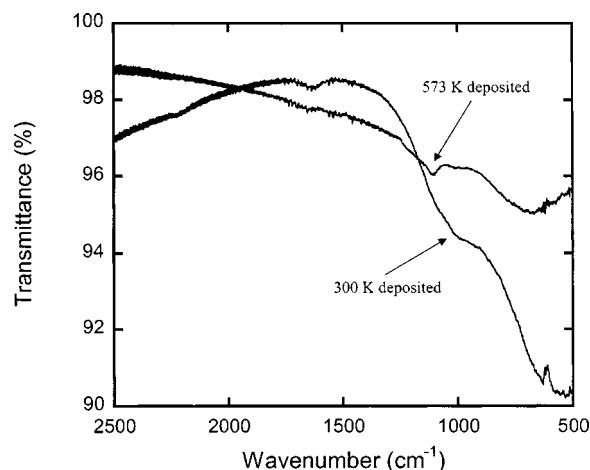


FIG. 2. FTIR spectra of the room-temperature and 573 K-deposited AlMgB₁₄ films.

that the former does not show any maze pattern, indicative of the amorphous structure in this film.

Figure 2 shows the FTIR spectra of AlMgB₁₄ films deposited at the two different substrate temperatures. For the room-temperature-deposited AlMgB₁₄ film, it can be seen that there is a weak absorption in the vicinity of 1000 cm⁻¹, which could be assigned to an overlapping of A_{2u} and E_u vibrational modes of a single B₁₂ icosahedron.¹² The low absorption intensity indicates that the B₁₂ icosahedron was not fully developed at this deposition temperature. For the AlMgB₁₄ film deposited at 573 K, however, a stronger absorption is observed at ~1100 cm⁻¹, which can be ascribed to the F_{1u} vibrational mode of a single B₁₂ icosahedron.¹³ This is a breathing mode characterized by two half-icosahedra vibrating against each other. The strong absorption intensity suggests that well-formed B₁₂ icosahedra are present in the 573 K-deposited AlMgB₁₄ film.

The measured hardness and moduli of the room-temperature and 573 K-deposited AlMgB₁₄ films are plotted in Fig. 3, 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.¹⁴ 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 3 shows that the maximum hardness for the room-temperature and 573 K-deposited AlMgB₁₄ 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 AlMgB₁₄ films.

Extraordinarily high hardness has been reported in superlattices and nanocomposite coatings, where interfacial phenomena govern the mechanical properties. Veprek *et al.*¹⁵ refer to such a microstructural contribution to hardness as extrinsic hardness. In this work, a superhardness of 45 GPa and 51 GPa was achieved for the room-temperature and 573 K-deposited AlMgB₁₄ films; however, it should be noted that such a high hardness was essentially obtained in an entirely amorphous structure, in which randomly distributed B₁₂

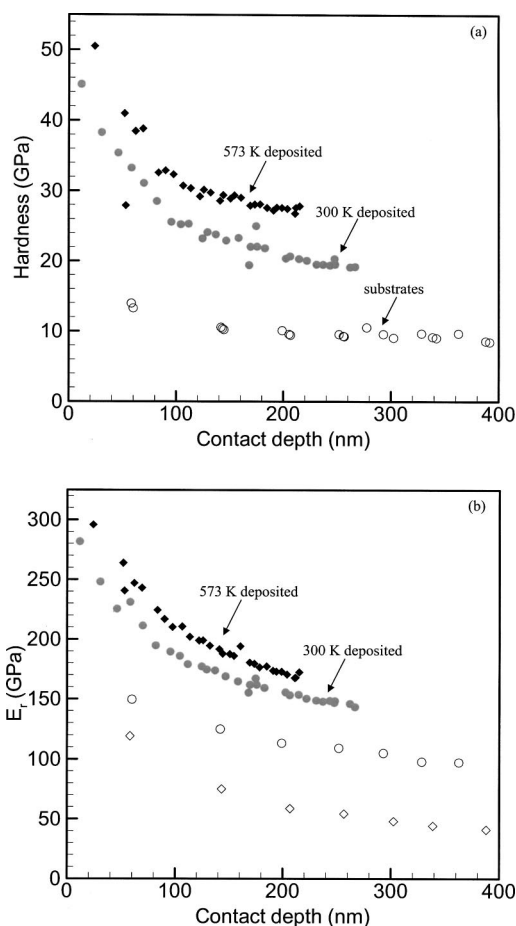


FIG. 3. (a) Hardness vs indentation contact depth for AlMgB₁₄ films on Si substrates. The hardness data of substrates were collected from a region of the substrates masked during deposition which consequently lacked any AlMgB₁₄ film. (b) Reduced moduli (E_r) vs indentation contact depth for AlMgB₁₄ films on Si substrates. 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 AlMgB₁₄ film.

icosahedra dominate according to the FTIR results. This appears to indicate that AlMgB₁₄ films derive their extreme hardness from the covalent, intraicosahedral B—B bonds, and the hardening mechanism for AlMgB₁₄ films should be considered as “intrinsic,” which is the case for conventional superhard materials, such as diamond and cubic-BN. The higher hardness (51 GPa) for the AlMgB₁₄ film deposited at 573 K may be due to its denser structure and the formation of more well-developed B₁₂ icosahedra at higher deposition temperatures, as indicated by the FTIR spectra.

What is scientifically intriguing about AlMgB₁₄ films is that the B—B bonding in B₁₂ icosahedra is indeed electron deficient.¹⁶ Consequently, the hardness is expected to be much lower than that of conventional superhard materials,¹⁷ whose crystal structures are typically based upon highly directional covalent sp^3 bonds. In this work, however, a hardness comparable to that of *c*-BN has been obtained in AlMgB₁₄ films. This anomaly might be associated with the incorporation of metallic dopants (i.e., Al and Mg) in

AlMgB₁₄ 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 AlMgB₁₄-type orthorhombic borides,¹⁸ leading to a full occupancy of valence band of B₁₂ icosahedra¹⁹ 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 AlMgB₁₄ films were found to be extremely low, ranging between 0.04 and 0.05. Such low friction behavior can be attributed to the *in situ* formation of a very lubricious surface layer of boric acid (H₃BO₃), which acts as a self-lubricant for AlMgB₁₄ films. Such compound has also been found on the surfaces of B₄C and borided steel.^{20,21}

In summary, we have demonstrated the growth of a superhard, self-lubricating AlMgB₁₄ film by PLD. Remarkable hardness of greater than 40 GPa was obtained from an entirely amorphous structure. In particular, AlMgB₁₄ film is a very promising candidate for protective coating on LIGA microdevices and Si-based MEMS components. Although thin films of B₄C and boron suboxide (B_xO, $x > 1$) have been studied for possible hard coating applications, this work examined the use of AlMgB₁₄ films for this purpose.

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