APPLIED PHYSICS LETTERS VOLUME 85, NUMBER 7 16 AUGUST 2004

Electrical transport in amorphous semiconducting $AlMgB_{14}$ films

Y. Tian[a)]
Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011

G. Li and J. Shinar
Ames Laboratory-USDOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011

N. L. Wang
Department of Electrical and Computer Engineering, Iowa State University, Ames, Iowa 50011

B. A. Cook and J. W. Anderegg
Ames Laboratory, United States Department of Energy, Ames, Iowa 50011

A. P. Constant, A. M. Russell, and J. E. Snyder
Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011

(Received 11 December 2003; accepted 15 June 2004)

The electrical transport properties of semiconducting $AlMgB_{14}$ films deposited at room temperature and 573 K are reported in this letter. The as-deposited films are amorphous, and they exhibit high *n*-type electrical conductivity, which is believed to stem from the conduction electrons donated by Al, Mg, and/or Fe impurities in these films. The film deposited at 573 K is less conductive than the room-temperature-deposited film. This is attributed to the nature of donor or trap states in the band gap related to the different deposition temperatures. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1781738]

Boron-rich boride films are refractory semiconductors, which have been the subject of intense investigation in recent years due to their attractive 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). Implementation of these materials will require a thorough understanding of their electrical properties, which are profoundly influenced by their composition,[6,7] microstructure,[5] and deposition methods.[8] Considerable research has focused on the electrical transport mechanism,[6] dielectric properties,[7] doping behavior,[9,10] and device performance[3,5] of boron compounds with C, N, and O, such as B_4C/B_5C, B_xN $(x>1)$ and boron suboxide $(B_xO, x>1)$. Recently, the ternary boride compound $AlMgB_{14}$ has attracted attention due to its interesting mechanical properties;[11,12] however, no studies have been reported on the electrical properties of $AlMgB_{14}$ thin films. This letter discusses the effect of deposition temperature 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 have an unusually low resistivity, and the charge carriers are predominantly *n* type.

The $AlMgB_{14}$ films were grown by pulsed laser deposition (PLD) from a hot-pressed $Al_{0.95}Si_{0.05}MgB_{14}$ target[11] on thermally oxidized Si (100) and Corning 7059 glass at room temperature and 573 K, respectively. The ambient pressure was maintained below 6×10^{-7} Torr. 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 a 5 h of baking at 100 °C, as indicated by room temperature current–voltage $(I-V)$ measurements. A hot probe method was also employed to determine the carrier type in $AlMgB_{14}$ films. The dark current I, at a constant voltage of 5 V, was recorded as a function of temperature T from 300 K to 453 K, with Al stripes made by thermal evaporation as contacts. The optical absorption spectra of the films grown on Corning 7059 glass were measured by a Perkin–Elmer ultraviolet-visible-near-infrared spectrophotometer. The optical band gaps were determined by fitting the optical absorption spectra to the Tauc equation.

PLD is considered a viable means of transferring target stoichiometry to thin films, and this has been confirmed by XPS analysis in the case of $AlMgB_{14}$ films. However, XPS measurements also indicated significant amounts of O and Fe in the films, which was discussed elsewhere.[13] XPS also indicated that there is no appreciable difference in composition between room-temperature- and 573 K-deposited $AlMgB_{14}$ films. The microstructure of $AlMgB_{14}$ films, which was examined by transmission electron microscopy,[12] remains amorphous regardless of substrate temperature, and no evidence of conducting inhomogeneities or crystalline domains was observed.

The electrical properties of the $AlMgB_{14}$ films are summarized in Table I. Compared with the electrical resistivity of other boron-rich boride films, which typically cover a wide range of values from $\sim10^3$ to 10^9 Ω cm, the electrical resistivity of room-temperature- and 573 K-deposited $AlMgB_{14}$ films is approximately three to eight orders of

---

[a)] Author to whom correspondence should be addressed; electronic mail: ytian@iastate.edu

TABLE I. The electrical properties of as-deposited Si-doped $AlMgB_{14}$ films.

Deposition temperature (K)	Resistivity (Ω cm) (four-point probe)	Resistivity (Ω cm) (van derPauw)	Carrier type	Carrier concentration (cm^{-3})	Carrier mobility ($cm^2/V\,s$)
300	4.4	4.5	*n*	2.85×10^{17}	4.86
573	38.2	41.1	*n*	2.06×10^{16}	6.89

magnitude lower, approaching that of single-crystal boron carbide.[10] Such low resistivity is particularly noteworthy since the films are entirely amorphous. Furthermore, the charge carriers in these $AlMgB_{14}$ films are dominated by electrons, as opposed to the holes which prevail in most boron-rich boride materials.

The low electrical resistivity observed in $AlMgB_{14}$ films is clearly a consequence of a high carrier concentration combined with moderate carrier mobility. In general, the electronic structure of all boron-rich boride materials is essentially determined by the B_{12} icosahedra. The valence band (VB) of these materials typically consists of an upper split-off subband VB_1, which is generated by the Jahn-Teller distortion of the B_{12} icosahedra, and a lower subband VB_2.[14] 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.[14] Moreover, strong electron–phonon coupling in B_{12} icosahedra leads to the formation of six intrinsic high-density trap levels within the band gap.[15] 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 *et al.*[16] reported an extremely high *n*-type carrier concentration ($\sim10^{21}$ cm^{-3}) and low carrier mobility (~0.133 $cm^2/V\,s$) associated with fine-grained, hot-pressed $AlMgB_{14}$, which they attributed to electron hopping mechanism.[16]

Neither electron hopping nor band conduction by holes can reasonably explain the unique transport behavior of the $AlMgB_{14}$ films. The significantly enhanced *n*-type carrier mobility observed in the films (4.86 and 6.89 $cm^2/V\,s$) suggests that it is the electrons, which are excited beyond the mobility edge into extended states of the conduction band,[17] that play a key role in the transport process of $AlMgB_{14}$ films. Moreover, the high carrier concentration (10^{16}–10^{17} cm^{-3}) suggests that these electrons are provided by metallic dopants in $AlMgB_{14}$ films, because pure boron films typically have far lower *p*-type carrier concentrations ($\sim10^{13}$ cm^{-3}).[18] There are two pathways to introduce dopants into the boron-rich boride materials: Substitution and network modification. The latter has been shown to occur with metallic dopants like Fe and Ni in boron carbide.[10] By network modification, metallic dopants simply fill the voids or interstitial positions in the B_{12} icosahedral network, and contribute their valence electrons to B_{12} icosahedra through charge transfer. The Al and Mg probably follow a similar mechanism in $AlMgB_{14}$ films as well. Fe impurities may also act as donors in these films, just as they do in boron carbide and β-rhombohedral boron.

Figure 1 shows ln *I* versus $1/T$ for the $AlMgB_{14}$ films. A well-defined linear behavior is evident, which is somewhat unusual given an amorphous semiconductor with complex composition, as such a "clean" doping behavior suggests that a single donor level is providing the conduction electrons. The activation energies are 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 introduce a donor level below the conduction-band edge. Due to the presence of minor amounts of Si (<1 at. %) in these films, the likelihood that Si is also a donor must be considered. Figure 2 shows ln *I* versus $1/T$ for baseline $AlMgB_{14}$ films, i.e., without Si. The activation energies are 0.11 eV for the room-temperature-deposited film

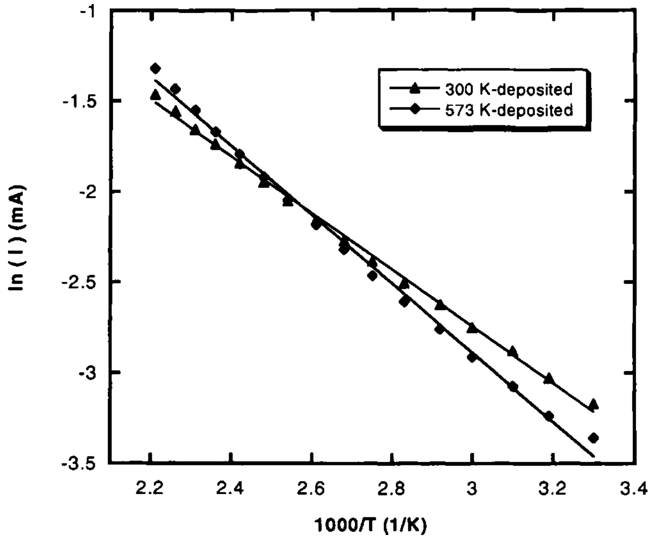

FIG. 1. ln *I* vs $1/T$ for the room-temperature- and 573 K-deposited Si-doped $AlMgB_{14}$ films.

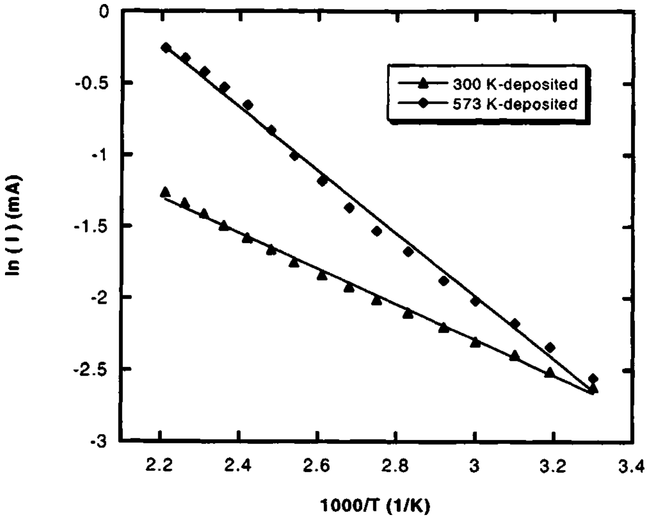

FIG. 2. ln *I* vs $1/T$ for the room-temperature- and 573 K-deposited baseline Si-free $AlMgB_{14}$ films.

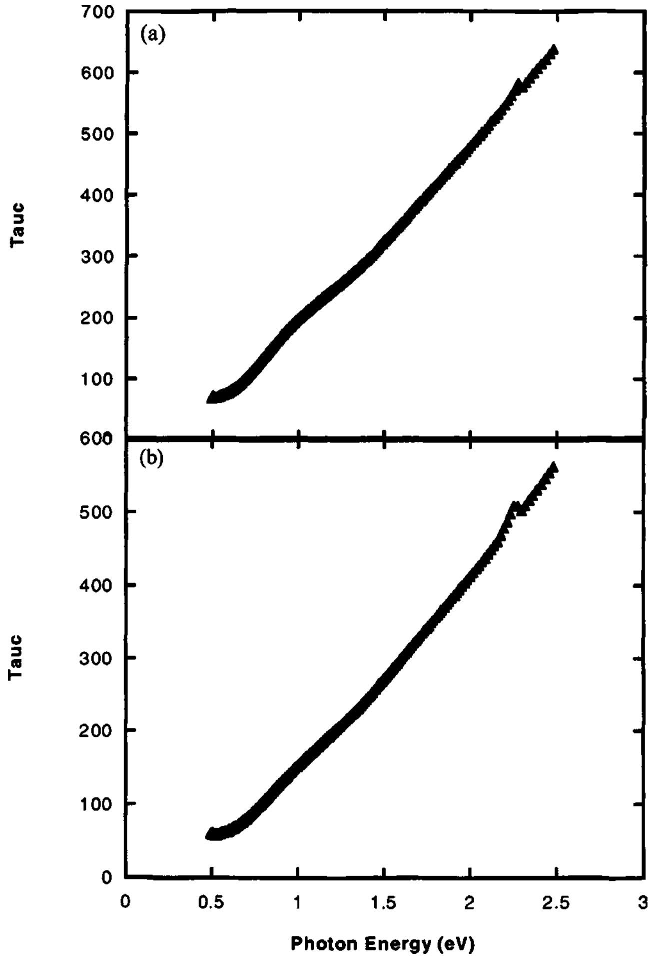

FIG. 3. Tauc plots of (a) the room-temperature-deposited Si-doped $AlMgB_{14}$ film and (b) the 573 K-deposited Si-doped $AlMgB_{14}$ film. The small peak in each plot is an absorption feature of the Corning 7059 glass.

and 0.19 eV for the 573 K-deposited film, suggesting that Si, however, does not have any impact on the transport properties of $AlMgB_{14}$ films, at least not to the extent of metallic atoms.

Transformation of intrinsically *p*-type boron-rich boride materials to *n*-type by doping is not a trivial task because of the difficulty in overcompensating for the high-density trap states in the band gap; an extremely high donor concentration, on the order of $\sim 10^{20}$ cm^{-3}, is generally required to enable this transformation.[19] In this study, however, *n*-type carriers were obtained in $AlMgB_{14}$ films at much lower donor concentrations. This is probably because the six intrinsic trap states, which basically depend on the vibrational modes of B_{12} icosahedra,[15] were not fully developed at the low deposition temperatures. Figure 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 the deposition temperature does not have a strong effect on the optical 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,[12] which, in turn, gives rise to more electron trap states in the gap. As the density of these trap states increases, a decrease in carrier concentration is expected, which is indeed observed in this study.

In summary, amorphous $AlMgB_{14}$ films produced by PLD show an unusually low resistivity. The high *n*-type carrier mobility demonstrates that the electrical transport is due mainly to band conduction by electrons, which are contributed by Al, Mg, and/or Fe donor states. The electrical properties of $AlMgB_{14}$ films are affected by the deposition temperature 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.

The work at Ames Laboratory was supported by the Director for Energy Research, Office of Basic Energy Science. Ames Laboratory is operated by Iowa State University for the U.S. Department of Energy under Contract No. W-7405-ENG-82.

[1] S. Lee, J. Mazurowski, G. Ramseyer, and P. A. Dowben, J. Appl. Phys. **72**, 4925 (1992).
[2] S. Hwang, D. Byun, N. J. Ianno, P. A. Dowben, and H. R. Kim, Appl. Phys. Lett. **68**, 1495 (1996).
[3] S. Hwang, K. Yang, P. A. Dowben, A. A. Ahmad, N. J. Ianno, J. Z. Li, J. Y. Lin, H. X. Jiang, and D. N. McIroy, Appl. Phys. Lett. **70**, 1028 (1997).
[4] C. Ronning, O. Wondratschek, M. Büttner, H. Hofsäss, J. Zimmermann, P. Leiderer, and J. Boneberg, Appl. Phys. Lett. **79**, 3053 (2001).
[5] S. Adenwalla, P. Welsch, A. Harken, J. I. Brand, A. Sezer, and B. W. Robertson, Appl. Phys. Lett. **79**, 4357 (2001).
[6] C. W. Ong, K. F. Chan, and C. L. Choy, Thin Solid Films **388**, 217 (2001).
[7] D. Music, V. M. Kugler, Z. Czigány, A. Flink, O. Werner, J. M. Schneider, L. Hultman, and U. Helmersson, J. Vac. Sci. Technol. A **21**, 1355 (2003).
[8] H. Suematsu, K. Kitajima, T. Suzuki, W. Jiang, K. Yatsui, K. Kurashima, and Y. Bando, Appl. Phys. Lett. **80**, 1153 (2002).
[9] S. Hwang, N. Remmes, P. A. Dowben, and D. N. McIroy, J. Vac. Sci. Technol. A **15**, 854 (1997).
[10] D. N. McIroy, S. Hwang, K. Yang, N. Remmes, P. A. Dowben, A. A. Ahmad, N. J. Ianno, J. Z. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. A: Mater. Sci. Process. **67**, 335 (1998).
[11] B. A. Cook, J. L. Harringa, T. L. Lewis, and A. M. Russell, Scr. Mater. **42**, 597 (2000).
[12] Y. Tian, A. F. Bastawros, C. C. H. Lo, A. P. Constant, A. M. Russell, and B. A. Cook, Appl. Phys. Lett. **83**, 2781 (2003).
[13] Y. Tian, A. Constant, C. C. H. Lo, J. W. Anderegg, A. M. Russell, J. E. Snyder, and P. Molian, J. Vac. Sci. Technol. A **21**, 1055 (2003).
[14] R. Schmechel and H. Werheit, J. Phys.: Condens. Matter **8**, 7263 (1996).
[15] H. Werheit and U. Kuhlmann, Solid State Commun. **88**, 421 (1993).
[16] T. L. Lewis, B. A. Cook, J. L. Harringa, and A. M. Russell, Mater. Sci. Eng., A **351**, 117 (2003).
[17] N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Materials* (Clarendon, Oxford, 1979), p. 220.
[18] Y. Kumashiro, T. Yokoyama, A. Sato, and Y. Ando, J. Solid State Chem. **133**, 314 (1997).
[19] Y. Kumashiro, *Electric Refractory Materials* (Marcel Dekker, New York, 2000), p. 591.