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

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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

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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 ($\sim0.133\ cm^2/V\,s$) 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

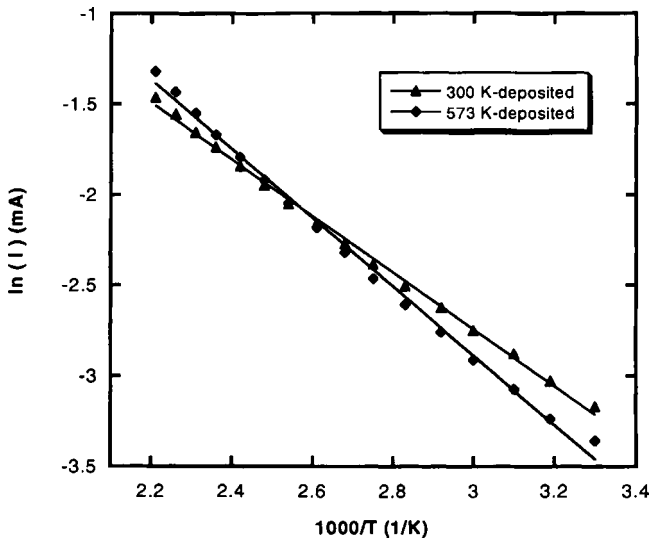

FIG. 1. $\ln I$ vs $1/T$ for the room-temperature- and 573 K-deposited Si-doped $AlMgB_{14}$ films.

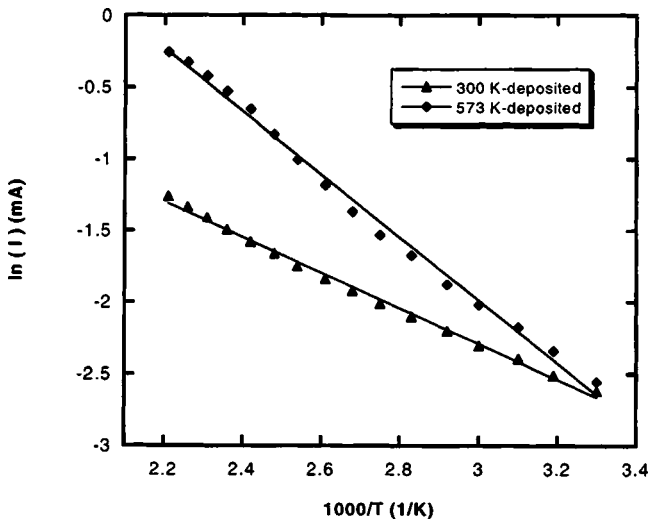

FIG. 2. $\ln I$ vs $1/T$ for the room-temperature- and 573 K-deposited baseline Si-free $AlMgB_{14}$ films.

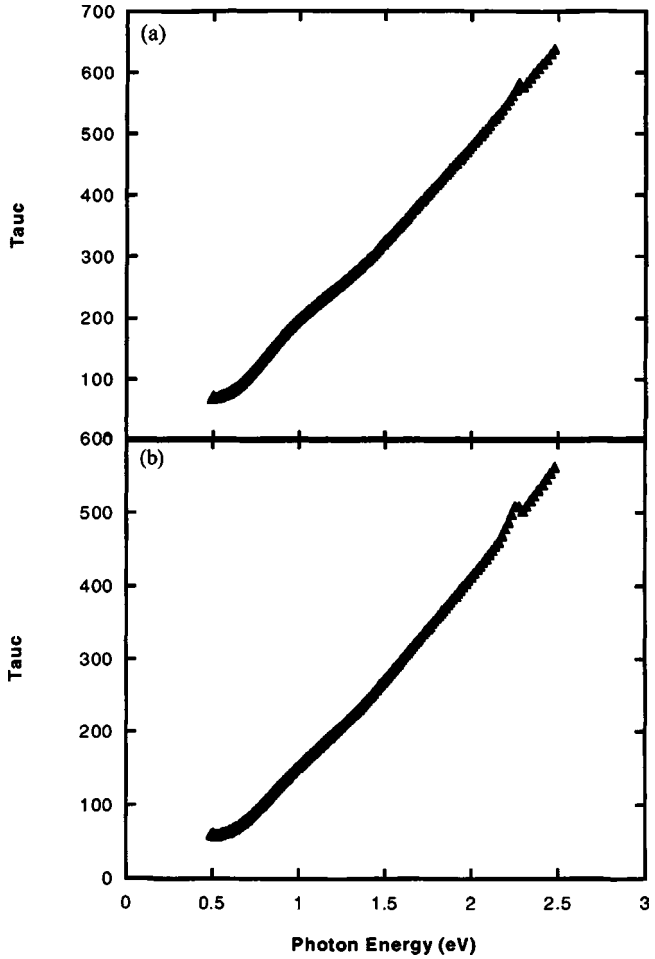

FIG. 3. Tauc plots of (a) the room-temperature-deposited Si-doped $AlMgB_{14}$ film and (b) the 573 K-deposited Si-doped $AlMgB_{14}$ film. The small peak in each plot is an absorption feature of the Corning 7059 glass.

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.

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