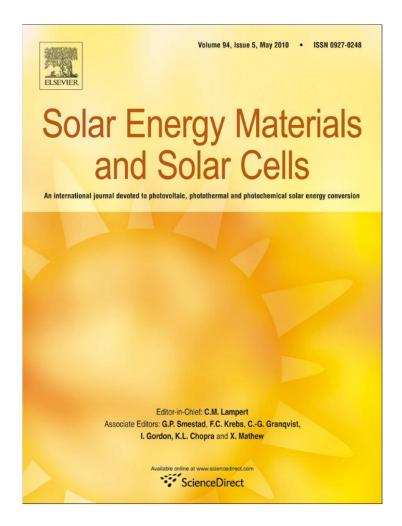
Provided for non-commercial research and education use. Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright

Solar Energy Materials & Solar Cells 94 (2010) 921-923

Contents lists available at ScienceDirect

# Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

# Low temperature deposited boron nitride thin films for a robust anti-reflection coating of solar cells

Andenet Alemu<sup>a,\*</sup>, Alex Freundlich<sup>a</sup>, Nacer Badi<sup>b</sup>, Chris Boney<sup>1,b</sup>, Abdelhak Bensaoula<sup>b</sup>

<sup>a</sup> Photovoltaic and Nanostructures Laboratory, Center for Advanced Materials, Departments of Physics, and Electrical and Computer Engineering, University of Houston, Houston, Texas 77204-5004, USA

<sup>b</sup> Nitride Materials and Devices Laboratory, Center for Advanced Materials, Departments of Physics, and Electrical and Computer Engineering, University of Houston, Houston, Texas 77204-5004, USA

#### ARTICLE INFO

Article history: Received 12 October 2009 Accepted 21 December 2009 Available online 23 February 2010

Keywords: Boron nitride Anti-reflection coating Gallium arsenide Silicon Solar cells Thin film

#### ABSTRACT

Polycrystalline boron nitride thin films deposited at low temperatures ( < 200 °C) are shown here to be well adapted for anti-reflection coating of solar cells. The analyses of the optical properties reveal a nearly constant index of refraction (~2.8) and negligible transmission losses over the useful range of the solar spectrum. Boron nitride thin films are found to be well adapted for integration as anti-reflection coating layers in multi-junction terrestrial and space solar cells due to their spectral stability, their robust ceramic nature and a fairly wide bandgap (6.2 eV). Test fabrication of double layer MgF2/BN anti-reflection coating on GaAs and Si demonstrated minimal reflection losses ( < 5%) over a wide window of the solar irradiance (1.1–3 eV).

© 2010 Published by Elsevier B.V.

Solar Energy Mater

#### 1. Introduction

The surface of common semiconductor solar cell materials such as silicon (Si) and gallium arsenide (GaAs) reflect back a significant portion of the incident sunlight ( $\sim$ 30%) [1,2]. These reflection losses are generally minimized by the use of anti-reflection coatings (ARC) that consist of one or more thin films carefully chosen for their thicknesses and refractive indexes and deposited on the top surface of solar cells [3,4]. Examples of commonly used ARCs in solar cell fabrication are oxides (silicon oxi-nitrides, TaO, etc.) and MgF2/ZnS. The latter is often used as a double layer ARC as it provides an ideal index match for solar cells with bandgaps ranging from 0.7-2 eV. A major shortcoming to most existing ARC schemes is the degradation of the device performance as a result of premature aging of ARC materials and the added complexity associated with protective encapsulation. It is highly desirable for an ARC material to be chemically inert and abrasion resistant for long duration (20-30 yr) exposure to natural elements. In addition, it's fabrication process (e.g. deposition temperature) must be compatible with that of solar cells and it must exhibit a high temperature stability and chemical compatibility with the solar cell material to avoid the

\* Corresponding author. Tel.: +1 713 7433621; fax: +1 713 7477724.

E-mail addresses: aalemu@uh.edu (A. Alemu), nbadi@uh.edu (N. Badi).

undesirable degradation (cross-diffusion, doping, sublimation,..) during high temperature welding/soldering of solar cell panels.

Boron nitride (BN) displays a wide bandgap of 6.2 eV. It is a ceramic material [5] with exceptional chemical and thermal stability [6] and hardness (comparable to diamond) [7]. BN layers have been used as high temperature dielectrics [8], electron field emitters [9], coatings for tribological applications [10], and as interfacial layers for optoelectronic devices [11]. However, the synthesis of high quality BN films is generally implemented at relatively high temperatures [12] that are marginally compatible with solar cell manufacture. In this work the optical properties of BN films deposited at relatively low temperature and their suitability for ARC application is investigated.

#### 2. Material and methods

Polycrystalline hexagonal BN thin films were grown on n-type GaAs (1 0 0) and Si (1 0 0) substrates in a high vacuum reactor by ion assisted physical vapor deposition at relatively low substrate temperatures (150 < T < 250 °C). An electron beam was used to evaporate high purity boron while a quartz crystal rate monitor was used to control the deposition. The nitrogen species were delivered by a gridless End Hall ion source (Commonwealth Scientific Mark II) fed with high purity (99.9999%) N<sub>2</sub>. The N<sub>2</sub> flow through the ion source was kept constant at 2.5 sccm and is proportional to the flux density of the nitrogen beam. It consists of



Letter

<sup>&</sup>lt;sup>1</sup> Also Integrated Micro Sensors, Inc., 10814 Atwell Dr., Houston, TX 77096.

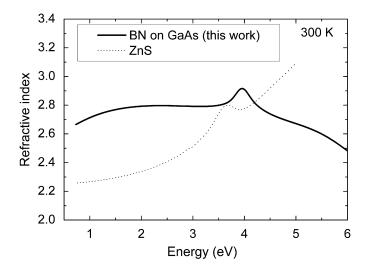
<sup>0927-0248/\$ -</sup> see front matter © 2010 Published by Elsevier B.V. doi:10.1016/j.solmat.2009.12.021

a mixture of  $N_2^+$  and  $N^+$  species with typical  $N_2^+/N^+=6$ . The ion beam current and energy were maintained at 110 mA and 45 eV, respectively. An evaporation rate of approximately 0.2 Å/s for boron yielded the maximum surface nitrogen content with high uniformity. *In situ* Auger electron spectroscopy (AES) measurement was performed to check the cleanness of the substrate prior to deposition. The surface stochiometry of deposited films was extracted from peak heights of the Auger KLL boron and nitrogen transitions [13]. A specular morphology with an RMS roughness of less than 2.5 nm was extracted from atomic force microscopy (AFM) analysis for the BN films prepared in these conditions.

The optical properties of BN/GaAs and BN/Si thin films were analyzed by spectroscopic ellipsometry using a J.A. Woollam M2000D ellipsometer. The wavelength dependency of the real (n) and imaginary (k) parts of the complex refractive index was extracted through direct comparison of the samples responses to those of GaAs and Si substrates. A model based on the effective medium approximation [14] was used to extract the films optical constants. The structural model included a thin "intermixing" layer representing a 50/50 mixture of the adjoining materials. The model also included a surface roughness layer, an intermix layer between the slightly non-planar surface of the film and the ambient.

## 3. Results and discussion

The wavelength dependency of the refractive index (n) and the extinction coefficient (k) of the fabricated BN film are represented in Fig. 1. The value of the BN refractive index (2.8 at 2 eV) for films deposited on GaAs or Si is slightly higher than those reported in the literature for cubic-BN (2.1 at 2 eV) and wurtzite-BN (2.05 at 2 eV) [15,16]. The refractive index remains somewhat constant over the 0.7-6 eV range (~2.7-2.9). It increases linearly from 2.7 to about 2.8 between 0.7 and 1.5 eV, where it reaches a plateau and remains constant up to 3.8 eV. It then increases to reach a value of 2.9 at 4 eV from which point it monotonically decreases to reach a value of 2.5 at 6 eV. For comparison purpose the index of refraction of ZnS thin film, which are commonly used in conjunction with MgF<sub>2</sub> for high-end efficiency demonstrator devices [17], is also represented. An interesting and promising aspect of this result comes from the fact that the refractive index of BN, unlike ZnS, stays fairly constant for a large span of the



**Fig. 1.** Energy dependence of the refractive indexes of BN films deposited at 200 °C on GaAs as extracted from ellipsometry measurements (solid line). For comparison purpose the index of refraction of ZnS (dashed line) is also represented.

electromagnetic spectrum, a welcome development that can lead to a lower and wider light transmission window. Surprisingly, these BN films exhibit a somewhat elevated extinction coefficient (Fig. 2), suggesting absorption of photons in the ultra violet. However, considering typical material thicknesses in ARC applications (50–100 nm) the resulting overall attenuation of the incident sunlight appears to be negligible.

The index of refraction of the BN films developed here appear to indicate that BN is an interesting candidate for use as an intermediate layer between the indexes of GaAs (3.94 at 2 eV [2–18] or Si (3.98 at 2 eV) [1] and those of cover glass (SiO<sub>2</sub>) or other low refractive index dielectrics [19]. To evaluate the suitability of BN for ARC applications, we have opted to use magnesium di-fluoride (MgF<sub>2</sub>, n=1.38 at 2.0 eV ) as a top component of the ARC. First a Fortran<sup>®</sup> based simulation code using a transfer matrix method similar to the one developed by Aroutiounian et al. [20] was implemented to predict the reflectance spectra of different thickness of ARC layers (BN, MgF<sub>2</sub>) deposited on different substrates (GaAs, Si). We then numerically evaluated the best layer thickness combination for BN and subsequent MgF<sub>2</sub> film by taking into account our experimental (n, k) values for BN films and those reported in the literature for MgF<sub>2</sub>[19], GaAs [18] and Si [1]. The predicted reduction of reflectance losses associated with the implementation of optimal MgF<sub>2</sub>/BN bilayer ARC deposited on GaAs (dotted black line) and Si (solid black line) are represented in Fig. 3 and compared to those of bare GaAs and Si (gray lines in Fig. 3).

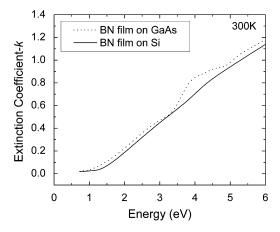
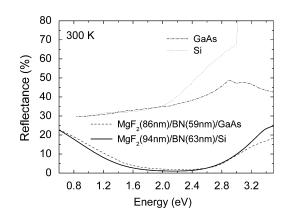


Fig. 2. Energy dependence of the extinction coefficient of BN films deposited on Si and GaAs as extracted from ellipsometry measurements.



**Fig. 3.** Reflectance simulations using measured *n* and *k* values for MgF<sub>2</sub> (940 Å)/BN (630 Å) on Si (solid black line) and MgF<sub>2</sub> (860 Å)/BN (590 Å) on GaAs (dashed black line). Si (dotted line) and GaAs reflectances (dashed and dotted line) as extracted from Refs. [1,2,19] are also represented.

A. Alemu et al. / Solar Energy Materials & Solar Cells 94 (2010) 921-923

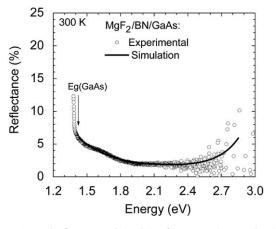


Fig. 4. Experimental reflectance and simulation for an  $MgF_2$  (100 nm)/BN (60 nm) anti-reflection coated GaAs sample.

In order to experimentally validate these predictions we fabricated a double layer MgF<sub>2</sub>/BN ARCs on GaAs and Si substrates using optimal sets of thickness as extracted from simulations. Following the deposition of 60 nm BN on GaAs and Si substrates, MgF<sub>2</sub> thin films ( $\sim$ 100 nm) were deposited by thermal evaporation of MgF<sub>2</sub> at a rate of 3 A/sec using a previously established procedure for the manufacture of space solar cells [21]. The corresponding reflectance spectra of the stacks were then measured by near-normal reflectance spectrometry. A tungsten halogen broad-spectrum white light source was used to illuminate the samples and the reflected light was focused at the entrance slit of a Jobin-Yvon® Triax 320 monochromator. A lockin technique was used to measure the intensity of the reflectance signal detected by a silicon photo detector placed at the exit slit of the monochromator. The useful range of the reflectance spectra was limited to below 2.7 eV due to the poor blue/UV spectral composition of the light source. The subsequent experimental reflectance analysis confirmed the predicted ARC attributes of MgF<sub>2</sub>/BN bilayers. An example of these analyses is shown in Fig. 4. The integrated reflective losses were found to be less than 3% over the 1.4-2.8 eV range (and less than 2% in the 1.8-2.5 eV window) demonstrating the effectiveness of the low temperature BN layers for ARC applications.

### 4. Conclusions

In summary, we have investigated the optical properties of BN films formed at relatively low temperatures and have experimentally demonstrated that these BN films are suitable, and in fact desirable, materials for anti-reflective applications of silicon and compound semiconductor photovoltaic materials. The inherent chemical, thermal, and structural stability and hardness make BN a material of choice for particularly hostile/harsh environments. In addition, these films could also be adapted to other optoelectronic applications.

#### References

- S. Adachi, Model dielectric constants of Si and Ge, Phys. Rev. 38 (1988) 12966–12976.
- [2] D.E. Aspnes, A.A. Studna, Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV, Phys. Rev. B 27 (1983) 985–1009.
- [3] A. Luque, S. Hegedus, in: Handbook of Photovoltaic Science and Engineering, John Wiley & Sons, 2003.
- [4] Taylor S.J., Leycuras A., Beaumont B., Coutal C., Roustan J.C., Azema A., in: Proceedings of 22nd IEEE Photovoltaic Specialist Conference, Waikolaa, Hawaii (1994): doi 10.1109/WCPEC.1994.520742.
- [5] N. Miyata, K. Moriki, O. Mishima, M. Fujisawa, T. Hattori, Optical constants of cubic boron nitride, Phys. Rev. B 40 (17) (1989) 12028–12029.
- [6] J.J. Pouch, S.A. Alterovitz, (Eds.), Synthesis and Properties of Boron Nitride, Materials Science Forum, Vols. 54 and 55, Trans Tech. Publications, Zurich, Switzerland, 1990, pp. 426.
- [7] N. Dubrovinskaia, V.L. Solozhenko, N. Miyajima, V. Dmitriev, O.O. Kurakevych, L. Dubrovinsky, Superhard nanocomposite of dense polymorphs of boron nitride: Noncarbon material has reached diamond hardness, Appl. Phys. Lett. 90 (2007) 101912.
  [8] N. Badi, C. Boney, A. Bensaoula, Self-packaged Boron Nitride Capacitor for
- [8] N. Badi, C. Boney, A. Bensaoula, Self-packaged Boron Nitride Capacitor for High Temperature Application, J. Micro. Elec. Pack. 1 (2004) 217–224.
  [9] N. Badi, A. Tempez, D. Starikov, A. Bensaoula, V.P. Ageev, A. Karabutov
- [9] N. Badi, A. Tempez, D. Starikov, A. Bensaoula, V.P. Ageev, A. Karabutov M.V. Ugarov, V. Frolov, E. Loubnin, K. Waters, A. Shultz, Field Emission from as-grown and Surface Modified BN and CN Thin Films, J. Vac. Sci. Technol. A 17 (1999) 1191–1195.
- [10] N. Badi, A. Tempez, J. Kulik, D. Starikov, N. Medelci, A. Bensaoula S.M. Klimentov, S.V. Garnov, V.P. Ageev, M.V. Ugarov, S. Lee, S.S. Perry K. Water, A. shultz, Boron Nitride Materials for Tribological and High Temperature High Power Devices, Mater. Res. Sos. Symp. Soc. 495 (1998) 358–366.
- [11] D. Starikov, N. Badi, I. Berichev, N. Medelci, O. Kameli, M. Sayhi V. Zomorrodian, A. Bensaoula, Metal-insulator-semiconductor Schottky Barrier Structures Fabricated Using Interfacial BN Layers Grown on GaN and SiC for Optoelectonic Device Applications, J. Vac. Sci. Technol. A 17 (1999) 1235–1238.
- [12] S.P.S. Arya, A. D'Amico, Preparation, properties and applications of boron nitride thin films, Thin Solid Films 157 (1988) 267–282.
- [13] A. Tempez, N. Badi, A. Bensaoula, J. Kulik, Surface composition of BN, CN, and BCN thin films, J. Vac. Sci. Technol. A 16 (1998) 2896–2900.
- [14] D.E. Aspnes, Optical properties of thin films, Thin Solid Films 89 (1982) 249-262.
- [15] P.J. Gielisse, S.S. Mitra, J.N. Plendl, R.D. Griffis, L.C. Mansur, R. Marshal E.A. Pascoe, Lattice Infrared Spectra of Boron Nitride and Boron Monophosphide, Phys. Rev. 155 (1967) 1039–1046.
- [16] M.E. Levinshtein, S.L. Rumyantsev, M.S. Shur (Eds.), Properties of Advanced Semiconductor Materials: GaN, AlN, InN, BN, SiC, and SiGe, John Wiley and Sons, New York, ISBN 0-471-35827-4, 2001.
- [17] J.F. Geisz, M.W. Sarah Kurtz, J.S. Wanlass, A. Ward, D.J. Duda, J.M. Friedman, W.E. Olson, T.E. McMahon, Moriarty, J.T. Kiehl, High-efficiency GaInP/GaAs/ InGaAs triple-junction solar cells grown inverted with a metamorphic bottom junction, Appl. Phys. Lett. 91 (2007) 023502.
- [18] S. Zollner, Optical constants and critical-point parameters of GaAs from 0.73 to 6.60 eV, J. Appl. Phys. 90 (2001) 515-517.
- [19] W.J. Tropf, Temperature-dependent refractive index models for BaF<sub>2</sub>, CaF<sub>2</sub>, MgF<sub>2</sub>, SrF<sub>2</sub>, LiF, NaF, KCI, ZnS, and ZnSe, Opt. Eng. 34 (1995) 1369–1373.
- [20] V.M. Aroutiounian, Kh. Martirosyan, P. Soukiassian, Low reflectance of diamond-like carbon/porous silicon double layer antireflection coating for silicon solar cells, J. Phys. D: Appl. Phys. 37 (2004) L25–L28.
   [21] A. Freundlich, F. Newman, M.F. Vilela, C. Monier, L. Aguilar, S. Street,
- [21] A. Freundlich, F. Newman, M.F. Vilela, C. Monier, L. Aguilar, S. Street, Development of GaAs space solar cells by high growth rate MOMBE/CBE, J. Cryst. Growth 209 (2000) 481–485.