J Mater Sci (2011) 46:5847–5850
DOI 10.1007/s10853-011-5541-5

Optical and electrical characteristics of amorphous boron carbonitride thin films deposited by radiofrequency sputtering

A. Essafti · E. Ech-chamikh

Received: 26 November 2010 / Accepted: 5 April 2011 / Published online: 14 April 2011

Abstract Amorphous boron carbonitride (a-BCN) thin films were deposited by reactive radiofrequency (RF) sputtering onto silicon and glass substrates, from a boron carbide target in an atmosphere composed of a mixture of argon and nitrogen. The a-BCN films were highly transparent (almost 85%) in the visible and near-infrared regions. The optical band gap and the refractive index in the near-infrared region of the a-BCN films were found to be, respectively, in the range of 3.6 and 1.68 eV. The electrical characterization of the a-BCN films for application as an intermetal dielectric was investigated by measuring the current–voltage characteristic in Al/a-BCN/*n*-Si/Al structure. The electrical resistivity at room temperature, determined in the low voltage region where the Ohmic conduction mechanism is dominant, is around $2 \times 10^{10}\ \Omega$ cm. The electrical conduction results, in the high-applied fields, were interpreted in terms of a Schottky mechanism. The dielectric constant is about 2.83 and is consistent with the optical results.

Introduction

In the past few years, there has been a growing interest in the production of boron carbonitride (BCN) films with high hardness for eventual use in mechanical applications. Although, the synthesis of a crystalline phase remains an open challenge and it requires of severe conditions to be grown. BCN material exhibits remarkable thermal stability, chemical inertness, high mechanical strength [1], large band gap [2], and excellent transmittance [3]. Therefore, such films can be used as protective coatings of optical components, in systems with high friction, and as insulators in electronic devices [4, 5]. This ternary material has been successfully synthesized by different techniques [6–9]. The electrical, mechanical, and optical properties of this system can be controlled by varying the C/B/N ratio. Depending on their composition and structure, BCN films are thought to be semiconductors or semi-metals [10]. Unlike the case of the study of mechanical properties of this material, the potential for optical and electronic application remains largely unexplored. Sputtering is one of the techniques commonly used to produce homogeneous thin films of high quality. Reactive radiofrequency (RF) sputtering is being explored to obtain new BCN films, stable in humid atmosphere and with excellent adherence to the substrates. A precise control of the experimental parameters can lead to obtain BCN films with a well-defined appropriate composition and structure, thus resulting in films with a high chemical stability and excellent properties. In this study, we report some optical and electrical properties of amorphous a-BCN thin films obtained by reactive RF sputtering from boron carbide (B_4C) target in an atmosphere composed of nitrogen and argon. A special attention is devoted to the electrical conduction mechanisms in a-BCN films deposited on silicon substrates. A correlation between the electrical and optical characteristics is presented also.

A. Essafti (✉) · E. Ech-chamikh
Laboratoire de Physique des Solides et des Couches Minces (LPSCM), Département de Physique, Faculté des Sciences Semlalia, Université Cadi Ayyad, B.P. 2390, 40000 Marrakech, Morocco
e-mail: aessafti@ucam.ac.ma

Experimental details

Amorphous boron carbonitride (a-BCN) thin films used in this study were deposited by reactive RF sputtering in an

ALCATEL SCM 451 deposition system equipped with an ALCATEL ARF 601 RF generator operating at 13.56 MHz. The a-BCN films were obtained from B_4C target with a purity of 99.5% in an atmosphere consisted of a mixture of high purity argon and nitrogen gas. The nitrogen partial pressure and the total pressure of the gas mixture were maintained, respectively, at 0.5 and 1 Pa. The RF power was fixed at 350 W. The samples were deposited during 4 h, at room temperature (i.e., without an intentional heating of the substrates), on silicon and glass substrates. The substrates were placed parallel to the target surface at a distance of 75 mm. The chemical study of these a-BCN films was reported in a previous study [11].

The optical transmittance, in the ultraviolet–visible–near-infrared wavelength range (between 200 and 2500 nm), was measured at room temperature and normal incidence using a double beam spectrophotometer (Shimadzu UV-3101 PC). The refractive index (n), the absorption coefficient (α), and the thickness of the a-BCN films were determined from the transmission spectra. Details concerning the determination of these parameters from the transmission spectrum, using the interferences fringes, have been reported by Swanepoel [12]. The Al/a-BCN/n-Si/Al structure was realized ex-situ after the exposure of the a-BCN/Si in the atmosphere. The back contact to n-type crystalline silicon (n-Si) substrate was made using Al, and the top contact was formed by thermal evaporation of Al dots with diameter of about 2 mm. The evaporation process of aluminum was carried out in a vacuum coating unit at about 10^{-3} Pa. The electrical current–voltage (I–V) characteristic, in the dark, was measured using a Kiethly 410 programmable picoamperemeter and a 610C programmable microvoltmeter. The electrical measurements were performed at room temperature.

Results and discussion

Optical properties

Figure 1 displays the optical transmittance spectrum of a-BCN thin film deposited on a glass substrate. This spectrum presents a high optical transmittance, in the visible and near-infrared regions, with an average value of 85%. This value is in the same order of that reported for nanocrystalline BCN films synthesized by plasma-assisted chemical vapor deposition [13]. The transmittance shows two distinct regions: one is the absorption edge and the other is beyond the absorption edge where the interference fringes appear. From this spectrum, which presents interferences fringes due to multiple reflections in film, we can deduce the film thickness, the variations of both the refractive index, and the absorption coefficient with wavelength. The thickness of this film as deduced from the transmittance spectrum is around 930 nm.

The inset of Fig. 1 represents the variation of the index of refraction of the a-BCN thin film, extracted from the optical transmittance spectrum, as a function of the wavelength. As can be seen, the refractive index decreases with increasing wavelength, and then remains constant for wavelength values higher than 1200 nm. The calculated values of the refractive index varies according with the dispersion Cauchy law of $n = A + \frac{B}{\lambda^2}$, where A and B are constants, and λ is the wavelength. The extrapolated refractive index in the near-infrared region (n_{IR}) of a-BCN film is in the order of 1.68. This low value is in accordance with the excellent transmittance of the a-BCN film shown previously.

It is well known that in an amorphous material characterized by indirect allowed transitions, the absorption coefficient (α) varies with the photons energy ($h\upsilon$) according to Tauc's relation [14]:

$$\sqrt{(\alpha h\upsilon)} = B(h\upsilon - E_G)$$

where B is constant, h is the Planck's constant, v is the frequency of incident photons, and E_G is the optical band gap. The variation of $(\alpha hv)^{1/2}$ as a function of hv, for a-BCN films, shows a linear behavior near the band gap (Fig. 2) as expected for amorphous materials. The E_G is given by the intercept of the straight line with the energy axis and is about 3.6 eV. Amorphous boron carbide, deposited in similar conditions with argon as sputtering gas, not presented in this figure, is characterized by an optical band gap of about 1.4 eV. This result indicates that the incorporation of nitrogen in the amorphous boron carbide networks increases the optical band gap. The E_G value is relatively higher than that reported by Lei et al. [15] for BCN material prepared by RF magnetron co-sputtering, but it is in the same range of the results found by Yang et al.

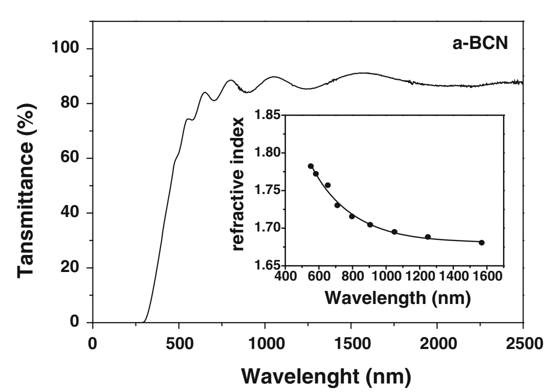

Fig. 1 Optical transmittance spectrum of a 930 nm thick a-BCN film deposited on glass substrate. The inset represents the refractive index for the same a-BCN film versus wavelength as deduced from the transmittance spectrum

[16] for BCN films prepared by laser ablation deposition in nitrogen atmosphere. Values of optical band gap between 4.4 and 3.7 eV were reported by Sulyaeva et al. [17] for BCN films prepared by plasma-enhanced chemical vapor deposition and they were dependent on the deposition temperature.

Electrical characterization

Figure 3 shows the *I–V* characteristic measured at room temperature for the Al/a-BCN/*n*-Si/Al structure in which the a-BCN film was deposited at the RF power of 350 W. It can be observed that the rectifying character for voltage was higher than 1.8 V. The inset represents the logarithmic plot of the forward *I–V* characteristic as obtained from the experimental data represented in Fig. 3. This characteristic suggests the existence of the Ohmic conduction mechanism ($I \propto V$) in the low-voltage region. In this region, we calculated the electrical resistivity at room temperature to be around 2×10^{10} Ω cm. This value indicates the insulator character of the a-BCN films and it is in the same order of that reported for polycrystalline BCN films synthesized by plasma-assisted chemical vapor deposition [18]. Electrical resistivity values of about 3–33 Ω cm were reported by Yao et al. [19] for BCN materials prepared by heat treatment under high pressure of amorphous BCN powders. These authors suggest that the behavior of the material is a semiconductor with a very small band gap. For higher voltages, we observe that the current exhibits a voltage dependence of the form $I \propto V^n$, where *n* changes and is found to be greater than unit. Consequently, this suggests that there are different types of conduction mechanisms: space charge limited current conduction mechanism and Schottky effect or Poole–Frenkel mechanism.

In order to determine the type of conduction mechanism we present in Fig. 4, the ln(*I*) versus ($E^{1/2}$) in the forward direction, where *E* is the applied electric field. A straight-

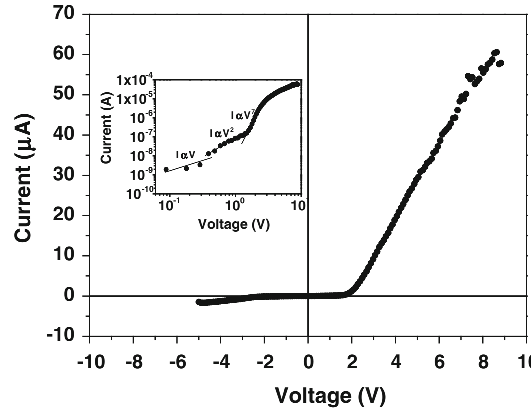

Fig. 3 Current–voltage characteristic at room temperature of the Al/a-BCN/*n*-Si/Al system. The inset shows the log(*I*) versus log*V*

line portion is observed at high-applied electric field, which can suggest that the conduction mechanism in the a-BCN film can be considered to be due to Schottky emission. The *I–V* characteristic of Schottky emission is of the form:

$$I = AT^2 S \exp\left[\frac{e}{kT}\left(\left(\frac{eE}{4\pi\varepsilon_o\varepsilon_r}\right)^{1/2} - \phi\right)\right]$$

where *T* is the absolute temperature, *k* is the Boltzmann constant, *e* is the charge of electron, ϕ is the barrier height, ε_r is dielectric constant of the insulator, ε_o is the permittivity of free space, *A* the Richardson constant, and *S* the area of contact. From the experimental slope 0.88×10^{-3} V/m$^{-1/2}$ of the straight-line portion in Fig. 4, we estimated the value of the dielectric constant ε_r of the a-BCN film to be 2.83 at 25 °C. This value is in the same order of that found by Yuki et al. [18]. We can also observe that the ε_r value is in agreement with the result of the refractive index *n* obtained in the previous section, according to $\varepsilon_r = n^2$ relation.

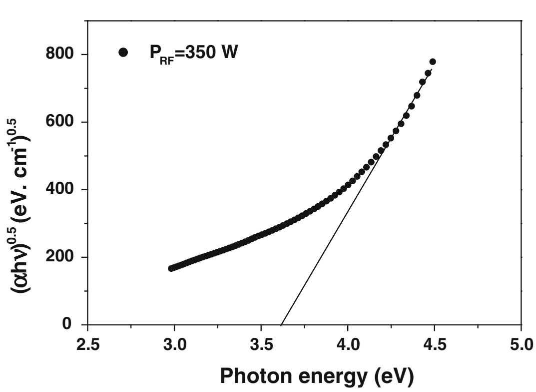

Fig. 2 The variation of $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ for a-BCN films

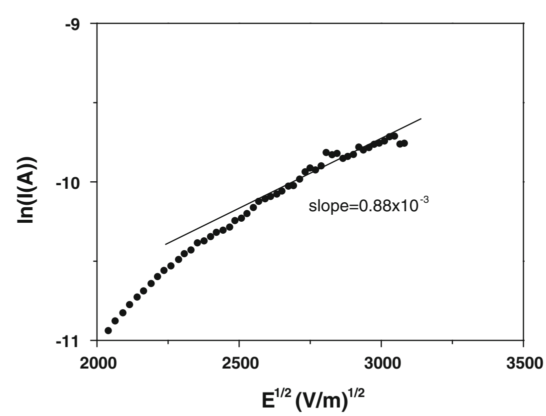

Fig. 4 Plot of ln(*I*) versus $E^{1/2}$ of the Al/a-BCN/*n*-Si/Al system in the forward direction at room temperature

Conclusion

Amorphous BCN films were deposited by RF sputtering from boron carbide target in a gas mixture of argon and nitrogen. The transmittance of the a-BCN films is very high (almost 85%) in the visible and near-infrared region. The refractive index and the optical band gap, as deduced from optical measurements, were about 1.68 and 3.6 eV, respectively. Finally, some insulating properties of the a-BCN films have been studied. *I–V* characteristic revealed that the dominant conduction mechanism at high-applied fields might be Schottky type. The dielectric constant, deduced from the Schottky conduction, was about 2.83 and it was consistent with optical results.

References

1. Morant C, Prieto P, Bareño J, Sanz JM, Elizalde E (2006) Thin Solid Films 515:2007
2. Aoki H, Ohyama K, Sota H, Seino T, Kimura C, Supino T (2007) Appl Surf Sci 254:596
3. Ahn H, Klimek KS, Rie K-T (2003) Surf Coat Technol 174–175:1225
4. Umeda S, Yuki T, Sugiyama T, Sugino T (2004) Diam Relat Mater 13:1135
5. Aoki H, Shima H, Kimura C, Sugino T (2007) Diam Relat Mater 16:1300
6. Gómez-Aleixandre C, Essafti A, Albella JM (2000) J Phys Chem B 104:4397
7. Popov C, Saito K, Ivanov B, Koga Y, Fujiwara S, Shanov V (1998) Thin Solid Films 312:99
8. Bai SZ, Yao B, Xing GZ, Zhang K, Su WH (2007) Physica B 396:214
9. Gago R, Jimenez I, Agullo-Rueda F, Albella JM, Czigany Zs, Hultman L (2002) J Appl Phys 92:5177
10. Yao B, Chen WJ, Liu L, Ding BZ, Su WH (1998) J Appl Phys 84:1412
11. Essafti A, Ech-chamikh E, Fierro JLG (2005) Diam Relat Mater 14:1663
12. Swanepoel R (1983) J Phys E Sci Instrum 16:1214
13. Cao ZX, Oeshner H (2003) J Appl Phys 93:1186
14. Tauc J, Menth A (1972) J Non-Cryst Solids 8–10:569
15. Lei MK, Li Q, Zhou ZF, Bello I, Lee CS, Lee TS (2001) Thin Solid Films 389:194
16. Yang Q, Wang CB, Zhang S, Zhang DM, Shen Q, Zhang LM (2010) Surf Coat Technol 204:1863
17. Sulyaeva VS, Rumyantsev YuM, Kosinova ML, Golubenko AN, Fainer NI, Kuznetsov FA (2007) Surf Coat Technol 201:9009
18. Yuki T, Umeda S, Sugino T (2004) Diam Relat Mater 13:1130
19. Yao B, Liu L, Su WH (1999) J Appl Phys 86:2464