Plasma enhanced chemical vapor deposition and characterization of boron nitride gate insulators on InP

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(Received 28 March 1991; accepted for publication 19 June 1991)

Thin films of boron nitride have been deposited in a plasma-enhanced chemical vapor deposition system, for use as a gate dielectric layer on InP. The InP substrates were pretreated by *in situ* HCl vapor etching prior to the film deposition. Borane-dimethylamine and ammonia were used as sources for boron and nitrogen. The depositions were carried out at low temperatures (320 °C), the samples being not directly exposed to the plasma which minimizes radiation damage to the substrates. The deposited films were characterized by ellipsometry, x-ray photoelectron spectroscopy, infrared and ultraviolet—visible spectroscopy. Metal-insulator-semiconductor structures were realized to evaluate the bulk dielectric and insulator—semiconductor interface properties. The growth rates are low (20 nm/h). X-ray photoelectron spectroscopy and infrared measurements showed that the layers are essentially boron nitride, with some boron excess (typically $N/B \approx 0.8$). The dielectric films were found to have an optical index $n \approx 1.7$, an optical band gap $E_0 \approx 5.8$ eV, a resistivity of about $10^{13} \Omega \text{ cm}$ and a dielectric constant of 3.5. Frequency dispersion, between 100 Hz and 1 MHz, of capacitance in accumulation did not exceed 10%. The interface state density was in the 10^{11} – $10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ range.

I. INTRODUCTION

In recent years indium phosphide (InP) and related materials have attracted much attention because these materials promise important approaches to a host of applications such as high speed integrated circuits, optoelectronic devices, microwave power devices, and so forth. Particularly considerable interest has been expressed in the study of technologies for insulator formation on InP,^{1,2} in order to realize metal-insulator-semiconductor field effect transistors (MISFETs). Various insulator materials and film deposition techniques have been used with a certain degree of success. However, these structures suffer from a lack of stability, which manifests itself by the drain current drift. In the case of silicon, the silicon based films SiO_2 and Si_3N_4 have been successfully used for all of the required applications, including passivation, insulation and encapsulation. On III–V compound semiconductors the above mentioned insulating films do not meet the requirements of some of these applications. Thus more extensive studies on forming several insulating films on InP are still required to improve the quality of the dielectric and the interface characteristics.

Boron nitride (BN) is a material which is known as being electrically insulating, chemically inert and thermally stable. Thus BN films can be useful for passivation, as gate dielectrics, diffusion sources of boron, sodium barriers, and as x-ray lithography masks.^{3,4} BN has been proposed as a gate dielectric for use with III–V

semiconductors,^{5–7} the most difficult and crucial application of an insulator film.

Several techniques have been used to deposit BN films, such as chemical vapor deposition (CVD), sputter deposition, ion beam deposition, reactive evaporation, pyrolysis, and so forth. The CVD technique is the most common and involves formation of reactive precursors by thermal means. These techniques generally require a high substrate temperature. Lowering of the deposition temperature is desirable for III–V compounds in order to reduce surface damage and therefore to maintain good metal-insulator-semiconductor (MIS) characteristics. With the aim of the deposition of BN on InP, we have developed a low temperature plasma enhanced chemical vapor deposition (PECVD) technique.⁸ By this technique, excitation of the reactants reduces the amount of thermal energy required compared to the conventional CVD process. It is thus possible to avoid excessive heating and subsequent degradation of the InP substrate, which is generally observed at temperatures higher than 350 °C. For BN deposition, the handling of toxic and hazardous starting materials, such as diborane, are often required in the thermal CVD technique. Here in order to avoid serious safety problems we use as source material borane-dimethylamine $\text{BH}_3\text{NH}(\text{CH}_3)_2$ (BDMA) which contains both nitrogen and boron. This compound becomes liquid around 36 °C and exhibits a relatively high volatility and substantial stability. Moreover, to improve the quality of the surface of

FIG. 1. Schematic diagram of the PECVD reaction system.

the InP samples, an *in situ* HCl vapor etching, prior to the BN deposition, has been implemented.

BN films obtained so far, prepared by CVD or PECVD have been either amorphous or in polycrystalline hexagonal form. The main parameter which governs the structure appears to be the substrate temperature whether the deposition technique is CVD or PECVD. Depositions at low substrate temperatures result in amorphous or in turbostratic films, whereas for higher temperatures polycrystalline material can be obtained.^{3,9} The chemical and physical properties of the layers are strongly dependent on the deposition parameters, as can be seen from a survey of the literature.^{3,4} The strong dependence of the properties of the BN films on the preparation conditions is mainly attributed to the composition and structure of the layers.

In this paper we describe the characterization of films deposited by PECVD at low substrate temperatures (320 °C). The composition of the films is analyzed by x-ray photoelectron spectroscopy (XPS). The optical properties of the films are studied in the ultraviolet-visible and infrared spectral regions, and by ellipsometry. Electrical properties of the films are evaluated by current-voltage (I-V) and capacitance-voltage (C-V) characteristics of MIS structures.

II. EXPERIMENT

The schematic diagram of the apparatus for the deposition of boron nitride is shown in Fig. 1. The pyrex reaction tube has an inside diameter of 6 cm and is 70 cm long. The substrates were placed on a graphite susceptor and heated by an external furnace. The substrate temperature was determined by a thermocouple embedded at the rear of the substrate holder. The pressure was measured with a capacitance manometer located at the exhaust end of the reaction tube. Between the reactor and the vacuum pump, cold traps are placed to condense the volatile reactants and products before they reach the pump. The RF power is supplied through capacitance coupling between electrodes outside the pyrex chamber. These electrodes are 14 cm long and can be moved along the pyrex reactor tube. It is thus possible to modify the relative position of the substrates and the plasma zone. When the samples are in intimate contact with the plasma, their surface is subjected to

electron, and ion bombardment which leads to some surface damage and consequently to a high interface state density in MIS structures. To minimize this effect, the samples were placed downstream the plasma zone, the distance between electrodes and substrates being typically 6–10 cm in this work.

The boron source compound is BDMA, which is heated up to 45 °C or 55 °C. Its vapor is transported by bubbling argon through the BDMA. This starting material contains in fact as much N as B, but the films obtained with BDMA alone exhibit a small N/B ratio.¹⁰ In order to approach a better stoichiometry for the deposited films it is necessary to add a nitrogen containing reactant. Thus ammonia is added into the system.

In a previous work⁸ it was found that the deposited layers contained a significant amount of oxygen. More than the contamination from the starting materials or from the residual gas, this could be attributed to the leak rate of the whole vacuum system. To decrease the leak rate of the apparatus only stainless-steel tubing is now used.

The substrates used in this experiment were undoped InP with (100) orientation. The samples were *n* type with a $2 \times 10^{15} \text{ cm}^{-3}$ carrier concentration. Before being loaded into the reaction chamber, the samples were chemically etched with a HCl solution (2 mol/l) for 5 min, to remove the oxide layer, then rinsed in deionized water and blown dry in nitrogen. In the reactor tube the substrates were kept under vacuum and then in pure N₂. The entire apparatus was repeatedly evacuated to about 10^{-2} mbar, and purged with N₂, whereas the temperature is progressively raised up to 180 °C. Water vapor adsorbed on the samples is removed during this process. The sample surface was etched *in situ* at 180 °C for 10 min with HCl vapor (35 cm³/min), diluted with N₂ (350 cm³/min), in order to eliminate the residual native oxide layer.¹¹ Then the reactor tube was heated up to the deposition temperature, 320 °C, in a pure N₂ flow. The deposition of the insulating layer was performed by introducing NH₃ and BDMA in Ar, the carrier gas. The flows were typically adjusted from 60 to 100 cm³/min for NH₃ and from 1.3 to 2 cm³/min for Ar. The whole pressure was adjusted to 1.5 mbar, by means of a valve located at the exhaust of the reactor. A plasma power at 13.56 MHz of about 50 W was then applied, and the RF matching network located between the RF generator and the plasma electrodes was adjusted to obtain a minimum reflected power, which corresponds to a maximally bright glow. After a deposition time of typically 2 hours, the plasma power was switched off and the samples were cooled under a flow of N₂. Besides the InP substrates, silicon and fused silica plates were also used, for XPS and IR studies, and UV-visible absorption measurements respectively.

III. RESULTS AND DISCUSSION

The thickness and refractive index of the deposited dielectric layers on InP and Si were measured ellipsometrically at a wavelength of 632.8 nm. The optical constants of InP and Si have been extracted from the values tabulated by Aspnes and Studna.¹² The growth rates are low

FIG. 2. Typical XPS diagram of BN film, with relative concentrations $N/B = 0.81$, $C/B = 0.49$ and $O/B = 0.15$.

ranging from 15 nm/h to 22 nm/h. The growth rate depends significantly on the distance of the substrates from the plasma zone. The index of refraction of the layers deposited on InP ranged from 1.68 to 1.73. For the films deposited on Si no significant difference could be detected. These values are close to those reported in the literature for BN coatings deposited with various techniques.^{7,9,13-16} Higher refractive indexes, from about 1.8 to 3, have been reported,^{9,17-19} and are generally attributed to a strong decrease in the nitrogen-to-boron ratio in the deposited layers. The small variations of the refractive index observed, suggest a relatively constant composition of our films.

The chemical analyses of the deposited layers were performed by x-ray photoelectron spectroscopy, with an Al anode. The oxygen impurities are in the 5–8 at% range and a substantial amount of carbon, up to about 20 at%, can be present in the layers. In all the cases investigated the films were boron rich with a relative N/B ratio ranging from 0.4 to 0.95. A representative XPS spectrum of one of the BN films is shown in Fig. 2. For this layer the relative concentrations are respectively $N/B = 0.81$, $C/B = 0.49$ and $O/B = 0.15$. The position of the peaks for B and N are coincident with published x-ray photoelectron data²⁰ for BN compounds. In fact the B_{1s} peak could be decomposed into two peaks. The main peak is characteristic of boron bonded to nitrogen, and shows that about 70%–80% of B is involved in BN. The second one is shifted by about 2 eV towards higher binding energies which can be attributed to a boron atom simultaneously bonded to oxygen and nitrogen,²¹ if compared with the shift reported for B_{1s} in B_2O_3 (≈ 3 eV).

Samples prepared on silicon substrates were used to observe the infrared spectra. A typical FTIR spectrum of a BN film, about 50 nm thick is shown in Fig. 3. The distinct features of the spectrum are a strong asymmetric band near 1380 cm^{-1} , and a weaker band at 790 cm^{-1} . The positions of these absorption peaks were practically the same for all the deposited layers. IR absorption measurements on BN films have been published by several

FIG. 3. FTIR spectrum of BN film.

workers.^{5,9,10,13,14,22-26} The two peaks are considered to correspond to those of the hexagonal form of BN.²⁷ The strong peak at 1380 cm^{-1} corresponds to B–N bond stretching and the weaker one at 790 cm^{-1} is attributed to B–N–B bending. No absorption at 2530 cm^{-1} , assigned to B–H stretching mode,¹⁰ or at 3430 cm^{-1} , assigned to N–H stretching mode,¹⁰ can be detected in our spectra. Only for thicker layers (of about 150 nm) deposited closer to the plasma zone, did we observe a slight and broad absorption band centered around 3400 cm^{-1} (the B–H peak at 2530 cm^{-1} being still missing). This broad absorption peak results from N–H groups (3400 and 3200 cm^{-1})¹⁷ and probably also from some O–H contribution. From these results we can conclude that our films deposited outside the plasma zone are essentially boron nitride, still containing probably some N–H bonds.

The optical absorption in the ultraviolet-visible region has been measured for layers deposited on fused silica substrates. The absorption coefficient α in the 190–300 nm band, of a BN film of thickness of about 45 nm is shown in Fig. 4. The absorption coefficient was determined by comparing the intensities of light passing through the film on the substrate and through the substrate alone, and further, the reflectance was not taken into account. The essential features of these results are the main absorption peak at 6.25 eV and a sharp drop up to 5.7 eV which has been attributed to the direct band gap. For lower photon energies the absorption coefficient has a finite value which can be related to the amorphous character of the films and to their imperfections. The optical band gap E_0 of the layers can be calculated from the plot of $(\alpha E)^2$ versus E , where $E = h\nu$ is the photon energy.⁹ Referring to the data shown in Fig. 5, and those obtained for other films, the energy gap is estimated to be between the values 5.8–5.9 eV. These values are in agreement with previous work on CVD films^{23,28-30} or on PECVD films,⁹ whereas lower values have been reported^{14,16} reaching even 3.8 eV.¹³ It has been suggested that E_0 decreases as the B concentration increases.¹⁶ The band gap for amorphous material is characterized by the local chemical environment. Therefore the excess B–B bonds narrow the optical band gap, which for

FIG. 4. Absorption coefficient of BN film as a function of the photon energy.

pure amorphous boron is about 1.3 eV.³¹ From these considerations our values are indicative of predominant B–N bonds.

To characterize the interface quality, Au/BN/InP MIS structures were fabricated: Au electrodes of 0.9 mm in diameter were evaporated onto the dielectric layers, whereas an ohmic contact to the back surface was obtained by thermal evaporation of eutectic Au–Ge followed by Au. Capacitance–voltage curves were recorded at frequencies

FIG. 5. Plot of $(\alpha E)^2$ vs E for the determination of the absorption edge E_0 .

FIG. 6. Capacitance–voltage characteristic at 1 MHz of a Au/BN/InP sample. The plot diameter was 0.9 mm, the bias sweep rate 100 mV/s and the BN thickness 40 nm. Dashed line, theoretical curve.

ranging from 100 Hz to 1 MHz and current–voltage characteristics were also determined. Figure 6 shows a typical C–V characteristic at 1 MHz of a MIS structure with a 40 nm thick BN layer. A gate voltage with a sweep rate of 100 mV/s was applied to the sample, starting from -3 V to $+3$ V and then back to -3 V. The results show a satisfactory capacitance modulation, and a clockwise hysteresis which indicates electron trapping at and near the surface, fast trapping centers being located essentially at the interface whereas slow centers are thought to be located in the insulating layer. The flat band voltage shift ΔV_{FB} , as a measure of the hysteresis, was about 0.3 V only, but the amount of hysteresis depends on the magnitude of the voltage excursion. For measurements performed between -5 and $+5$ V, with the same bias sweep rate of 100 mV/s, ΔV_{FB} could reach 1 V, resulting from charges trapped in the dielectric layer near the interface. The overall shift of the curves towards positive voltage, as compared with an ideal C–V curve, corresponds mainly to fixed negative charges located in the bulk of the insulator layer or at the insulator–semiconductor interface. By using the data for accumulation capacitance, the mean value of the dielectric

FIG. 7. Frequency dispersion of capacitance with applied voltage (100 mV/s) from 100 Hz to 1 MHz. Only curves from accumulation to inversion are shown.

constant could be estimated to be about 3.5, in agreement with previous reported values,^{5,9,13} but higher values have also been found.^{7,8,14,22} An estimation of the interface state density distribution can be obtained from the 1 MHz C-V curves by applying the Terman method. We obtained a minimum interface state density distribution varying from 2×10^{11} to $6 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ for different samples.

Figure 7 shows C-V characteristics recorded at different frequencies with a sweep rate of 100 mV/s. Only left-going curves are reported for clarity. Frequency dispersion is essentially observed in accumulation. The frequency dispersion for accumulation capacitance, from 100 Hz to 1 MHz, does not exceed 10% for most of the structures investigated.

From the measured I-V characteristics, a rough estimation of the resistivity of the insulating layers can be given. It is found that the resistivity ranges from 10^{13} to about $5 \times 10^{13} \Omega \text{ cm}$.

IV. CONCLUSIONS

In the present work, improved PECVD of boron nitride on InP was carried out, as compared to our previous results.⁸ A lower leakage rate of the whole apparatus resulted in layers with smaller oxygen contamination. Nevertheless, there remains a significant amount of carbon originating from the organometallic precursor. *In situ* HCl vapor etching of the InP substrates was carried out in order to remove the native oxide layer before the deposition process. The dielectric layers were identified as being essentially BN by XPS and IR measurements. This was also corroborated by optical absorption measurements in the ultraviolet-visible region which led to $E_0 \approx 5.8 \text{ eV}$ for the optical band gap. The resistivities of the layers are better than about $10^{13} \Omega \text{ cm}$. The C-V characteristics exhibit large capacitance variations, and consequently a satisfactory modulation of the surface potential of the semiconductor can be obtained. About 10% frequency dispersion of the C-V curves appears, between 100 Hz and 1 MHz, in accumulation. Finally the interface state density evaluated at 1 MHz by the Terman method, is in the 10^{11} – $10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ range.

- ¹J. F. Wager, S. J. T. Owen, and S. J. Prasad, *J. Electrochem. Soc.* **134**, 160 (1987).
- ²P. Viktorovitch, *J. Electrochem. Soc.* **136**, 1431 (1989).
- ³E. Yamaguchi, *Mater. Sci. Forum* **54–55**, 329 (1990).
- ⁴R. T. Paine, C. K. Narula, *Chem. Rev.* **90**, 73 (1990).
- ⁵W. Schmolla and H. L. Hartnagel, *Solid-State Electron.* **26**, 931 (1983).
- ⁶W. Schmolla, *Intern. J. Electron.* **58**, 35 (1985).
- ⁷E. Yamaguchi and M. Minakata, *J. Appl. Phys.* **55**, 3098 (1984).
- ⁸A. Bath, P. J. Van der Put, J. Schoonman, and B. Lepley, *Appl. Surface Sci.* **39**, 135 (1989).
- ⁹T. H. Yuzuriha and D. W. Hess, *Thin Solid Films* **140**, 199 (1986).
- ¹⁰D. M. Schleich, W. Y. F. Lai, and A. Lam, *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*, NATO ASI Ser. E, edited by R. M. Laine (Martinus Nijhoff, 1988), Vol. 148, pp. 178–184.
- ¹¹Y. Hirota, M. Okamura, and T. Kobayashi, *J. Appl. Phys.* **53**, 536 (1982).
- ¹²D. E. Aspnes and A. A. Studna, *Phys. Rev. B* **27**, 985 (1983).
- ¹³M. J. Rand and J. F. Roberts, *J. Electrochem. Soc.* **115**, 423 (1968).
- ¹⁴H. Miyamoto, M. Hirose, and Y. Osaka, *Jpn. J. Appl. Phys.* **22**, L216 (1983).
- ¹⁵J. Szmids, A. Jakubowski, and A. Balasinski, *Thin Solid Films* **142**, 269 (1986).
- ¹⁶J. J. Pouch, S. A. Alterovitz, K. Miyoshi, and J. D. Warner, *Mat. Res. Soc. Symp. Proc.* **93**, 323 (1987).
- ¹⁷A. C. Adams and C. D. Capio, *J. Electrochem. Soc.* **127**, 399 (1980).
- ¹⁸C. Kim, B. K. Sohn, and K. Shono, *J. Electrochem. Soc.* **131**, 1384 (1984).
- ¹⁹R. A. Levy, D. J. Resnick, R. C. Frye, A. W. Yanof, G. M. Wells, and F. Cerrina, *J. Vac. Sci. Technol. B* **6**, 154 (1988).
- ²⁰*Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer, Physical Electronics Industries, Eden Prairie, MN, 1979).
- ²¹O. Dugne, S. Prouhet, A. Guette, R. Naslain, R. Fourmeaux, K. Hssein, J. Sevely, C. Guimon, D. Gonbeau, and G. Pfister-Guillouzo, *J. Physique Coll.* **50**, C5 333 (1989).
- ²²S. B. Hyder and T. O. Yep, *J. Electrochem. Soc.* **123**, 1721 (1976).
- ²³K. Nakamura, *J. Electrochem. Soc.* **132**, 1757 (1985).
- ²⁴S. Komatsu, K. Akashi, and T. Yoshida, *ISPC-7 Eindhoven paper number P-5-11*, p. 142 (1985).
- ²⁵P. Lin, C. Deshpandey, H. J. Doerr, R. F. Bunshah, K. L. Chopra, and V. Vankar, *Thin Solid Films* **153**, 487 (1987).
- ²⁶A. Chayahara, H. Yokoyama, T. Imura, Y. Osaka, and M. Fujisawa, *Jpn. J. Appl. Phys.* **27**, 440 (1988).
- ²⁷R. Geick, C. H. Perry, and G. Rupprecht, *Phys. Rev.* **146**, 543 (1966).
- ²⁸A. Zunger, A. Katzir, and A. Halperin, *Phys. Rev. B* **13**, 5560 (1976).
- ²⁹M. Sano and M. Aoki, *Thin Solid Films* **83**, 247 (1981).
- ³⁰K. Nakamura, *J. Electrochem. Soc.* **133**, 1120 (1986).
- ³¹K. Nakamura, *J. Electrochem. Soc.* **131**, 2691 (1984).