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Plasma enhanced chemical vapour deposition of boron nitride onto InP

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Abstract

A low temperature plasma enhanced chemical vapour deposition technique was used to grow thin boron nitride films on indium phosphide. The starting materials were ammonia and borane-dimethylamine, the carrier gas being pure hydrogen. The films were characterized by ellipsometry, X-ray photoelectron spectroscopy (XPS) and IR spectroscopy. The electrical properties of the insulator–semiconductor interface were analysed by capacitance–voltage measurements and deep level transient spectroscopy. The deposited layers were identified as being essentially boron nitride, in the hexagonal form, by XPS and IR measurements. Good capacitance modulation was observed with a minimum interface state density distribution of about 5×10^{11} cm^{-2} eV^{-1}.

1. Introduction

Boron nitride (BN) is well known as being electrically insulating and chemically and thermally stable. Much work has been done on synthesizing this material [1, 2] in thin film form. Recent years have also seen an increasing interest in cubic phase BN, which may be a promising alternative to diamond for many applications [3–5]. Despite these advances, there is still a need for improved deposition processes, particularly those which would allow the growth of BN films at lower substrate temperatures. The importance of low temperature processing techniques in the fabrication of advanced semiconductor devices has been recognized for many years. Thus several technologies for the formation of insulators on semiconductors have been developed and, among the possible insulators, BN has been proposed as a gate dielectric for use with III–V semiconductors [6–9].

In this paper we describe the characterization of films deposited by plasma enhanced chemical vapour deposition (PECVD) at low temperature onto indium phosphide (InP), hydrogen being used as the carrier gas for the liquid organic source material. The electrical properties of the boron nitride–InP substrate interface were evaluated by capacitance–voltage measurements and deep level transient spectroscopy measurements performed on MIS (metal–insulator–semiconductor) structures.

2. Experimental details

The films were deposited with essentially the same plasma enhanced CVD system described in previous papers [9, 10]. The reactor itself is a glass tube, provided with external cylindrical r.f. electrodes. The samples were placed on a graphite susceptor located downstream of the plasma region in order to minimize surface damage. Heating was achieved by an external furnace and the temperature was monitored with a thermocouple embedded in the graphite susceptor. As boron source, B_2H_6 has often been used, but we preferred borane amines which contain both boron and nitrogen and are less dangerous to handle. Thus BH_3-$NH(CH_3)_2$, borane-dimethylamine (BDMA), was used. In order to obtain better stoichiometry of the deposited films, NH_3 was added to the system. In this work the BDMA, which becomes liquid at about 36 °C, was heated up to 45 °C and pure hydrogen was used as the carrier gas to transport its vapour into the reaction chamber. To avoid premature reaction, the reactant gases are brought into the reactor separately. The films were typically produced at a temperature of 320 °C, with a flow of about 40 cm^3 min^{-1} for NH_3, and adjusted from 6 to 100 cm^3 min^{-1} for H_2. The total pressure was maintained at 1.5 mbar.

The substrates used in this work were undoped n-Inp of (100) orientation, with a carrier concentration of about 5×10^{15} cm^{-3}. Before film deposition, the sample

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surface was etched *in situ* with HCl vapour at 180 °C to remove the native oxide layer [9]. A plasma power of 50 W at 13.56 MHz was then applied, the deposition time being typically 2 h. Silicon substrates were also used for IR studies.

3. Results and discussion

The films exhibit good adhesion to the substrates and appear very smooth under a scanning electron microscope. The refractive index and the thickness of the films were determined by ellipsometry at 633 nm. For the BN films an extinction coefficient $k = 0$ was assumed, and for the optical constants of the substrates (InP and Si), the values reported by Aspnes and Studna [11] were used. The refractive index of the deposited layers ranged from 1.72 to 1.78 which corresponds well with the values reported for amorphous boron nitride with a B-to-N-ratio of approximately unity [1, 12]. Growth rates ranged from 20 nm h^{-1} to 50 nm h^{-1}, the main parameter being the amount of reactant gas introduced in the reactor.

The chemical composition of the deposited films, determined by X-ray photoelectron spectroscopy (XPS) with an aluminium anode, is typically close to stoichiometric BN, with substantial amounts of oxygen and carbon. Figure 1 shows an XPS survey from the surface of an as-received BN film deposited onto silicon. The binding energies of the B 1s and N 1s are coincident with published X-ray photoelectron data [13] for BN, with very similar ratios of peak heights. The oxygen concentration does not exceed 5 at.%, whereas a smaller but still significant amount of carbon ($\simeq 15$ at.%), as compared with previous work [9], is observed. The relative concentration [N]/[B] is 0.82, a value which is representative of the analysed films. The B 1s and N 1s peaks, shown in Fig. 2, are nearly symmetrical peaks at binding energies of 190.1 eV and 398.6 eV respectively, with full widths at half-maximum of 2.2 eV for the two peaks. These results suggest that B and N atoms are involved essentially in BN bonds [13–15].

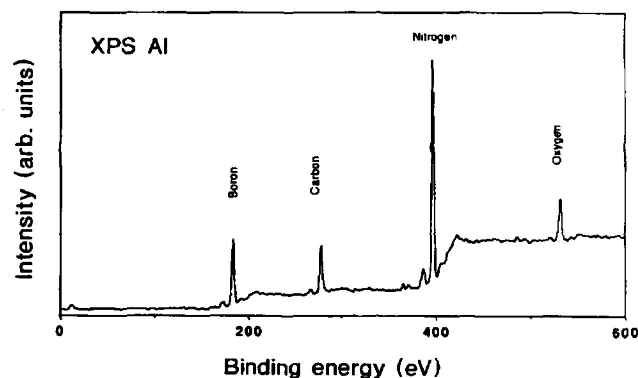

Fig. 1. XPS spectrum of an as-received BN film with relative concentrations [N]/[B] = 0.82, [C]/[B] = 0.35 and [O]/[B] = 0.11.

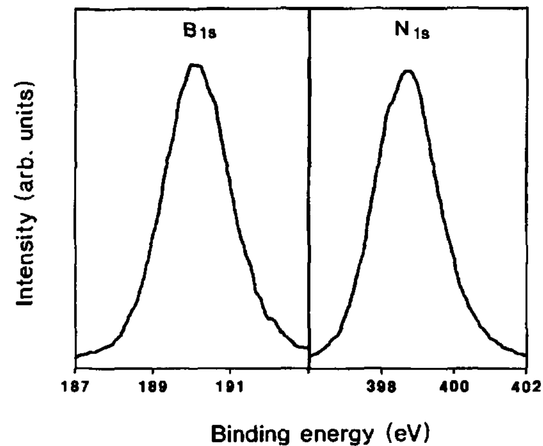

Fig. 2. B 1s and N 1s XPS spectra.

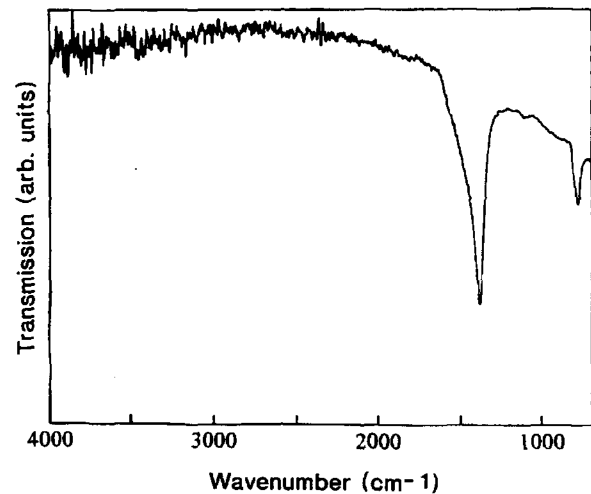

Fig. 3. IR transmission spectrum of boron nitride films deposited onto silicon.

Figure 3 shows a typical FTIR spectrum. The main features which were observed for all deposited layers are a strong asymmetric absorption band at 1380 cm^{-1} and a weaker band near 790 cm^{-1}. These two peaks are attributed to the in plane and out of plane vibration modes respectively [16, 17] of the hexagonal form of BN. No absorption due to B–H (≈ 2500 cm^{-1}) or N–H groups (≈ 3400 cm^{-1}) is observed. Slight absorption due to N–H groups was found only for a few layers.

To assess the interface quality, MIS structures were fabricated. The ohmic contact was formed on the back surface on the InP samples before deposition by sequential thermal evaporation of Au–Ge eutectic alloy

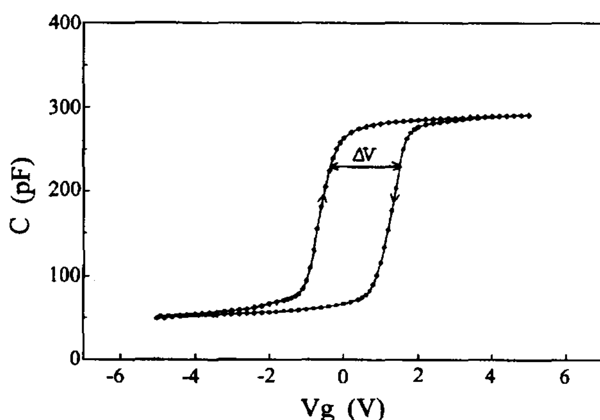

Fig. 4. Capacitance-voltage characteristic at 1 MHz of an MIS structure; bias sweep rate 100 mV s^{-1}, insulator thickness 98 nm.

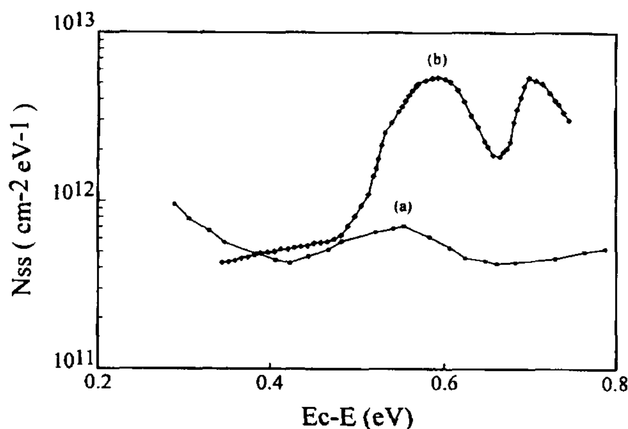

Fig. 6. Distribution of the interface density of states of an MIS structure deduced from (a) the Terman method and (b) DLTS.

and gold. Evaporated gold was used for the top electrode. From current-voltage measurements it was found that the resistivity of most deposited layers is in the $10^{11}-10^{12}$ Ω cm range. Capacitance-voltage curves were recorded at different frequencies. A typical plot of capacitance *vs.* voltage at 1 MHz is shown in Fig. 4, for an MIS structure with an insulator thickness of 98 nm. The bias sweep rate was fixed at 100 mV s^{-1}. The recorded curves show a satisfactory capacitance modulation, and a clockwise hysteresis which may be associated with electron trapping and detrapping at and near the interface. The hysteresis voltage shift ΔV is 2 V. The amount of hysteresis naturally depends on the magnitude of the voltage excursion. For a sweep voltage in the range -10 V to $+10$ V, with the same sweep rate of 100 mV s^{-1}, a value of $\Delta V = 3.5$ V was obtained. Figure 5 shows capacitance-voltage characteristics measured with frequencies ranging from 200 Hz to 1 MHz. The frequency dispersion of the capacitance can be seen

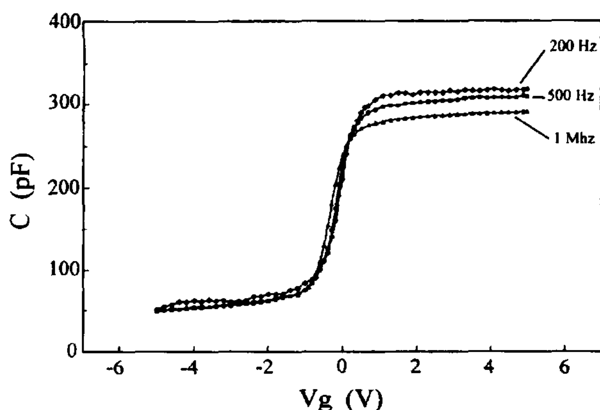

Fig. 5. Frequency dispersion of capacitance, from 200 Hz to 1 MHz; bias sweep rate 100 mV s^{-1}. Only curves from inversion to accumulation are shown.

especially in the accumulation region, and is about 10%.

The interface state density N_{ss} was deduced from the 1 MHz capacitance-voltage curve, using the Terman method. The result is presented in Fig. 6 (curve a). In the upper half band gap, the interface state density remains below 10^{12} cm^{-2} eV^{-1}, the minimum value being 5×10^{11}, with a broad peak located at about 0.55 eV below the conduction band minimum. The distribution of the interface state density was also investigated using deep level transient spectroscopy (DLTS). The result obtained for the same structure is reported in Fig. 6 (curve b). The distributions of interface states deduced from both methods present the same order of magnitude near the conduction band, whereas the DLTS measurements give a rather higher N_{ss} value in the region around 0.6 eV below the conduction band. The differences in the results obtained by both methods can be attributed mainly to the limitations involved in the Terman method.

4. Conclusions

Boron nitride films were deposited onto InP by a PECVD technique using the reaction of ammonia and BDMA, and hydrogen as carrier gas. Comparison with previous work [9], performed without hydrogen can be summarized as follows. The presence of H_2 during film deposition results in a decrease in the amount of O and C in the films. The layers remain slightly boron rich, yet a better stoichiometry was regularly approached during these experiments. The interface quality of the structures has not been significantly improved, and is comparable with that obtained previously. On the whole, MIS capacitors based on these layers exhibit encouraging behaviour.

References

1 S. P. S. Arya and A. D'Amico, *Thin Solid Films, 157* (1988) 267.
2 R. T. Paine and C. K. Narula, *Chem. Rev., 90* (1990) 73.
3 G. L. Doll, J. A. Sell, C. A. Taylor II and R. Clarke, *Phys. Rev. B, 43* (1991) 6816.
4 D. J. Kester and R. Messier, *J. Appl. Phys., 72* (1992) 504.
5 M. Okamoato, Y. Utsumi and Y. Osaka, *Jpn. J. Appl. Phys., 31* (1992) 3455.
6 W. Schmolla and H. L. Hartnagel, *Solid-State Electron., 26* (1983) 931.
7 E. Yamaguchi and M. Minakata, *J. Appl. Phys., 55* (1984) 3098.
8 V. J. Kapoor and G. G. Skebe, *Mater. Sci. Forum, 54–55* (1990) 353.
9 A. Bath, P. J. van der Put, J. G. M. Becht, J. Schoonman and B. Lepley, *J. Appl. Phys., 70* (1991) 4366.
10 J. G. M. Becht, A. Bath, E. Hengst, P. J. van der Put and J. Schoonman, *J. Phys. (Paris) IV, 1* (1991) C2-617.
11 D. E. Aspnes and A. A. Studna, *Phys. Rev B, 27* (1983) 985.
12 S. S. Dana, *Mater. Sci. Forum, 54–55* (1990) 229.
13 *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, MN, 1979.
14 H. Saitoh, K. Yoshida and W. A. Yarbrough, *J. Chem. Vapor Deposition, 1* (1992) 59.
15 N. Patibandla and K. L. Luthra, *J. Electrochem. Soc., 139* (1992) 3558.
16 R. Geick, C. H. Perry and G. Rupprecht, *Phys. Rev., 146* (1966) 543.
17 T. H. Yuzuriha and D. W. Hess, *Thin Solid Films, 140* (1986) 199.