Applied Surface Science 39 (1989) 135-140
North-Holland, Amsterdam

STUDY OF BORON NITRIDE GATE INSULATORS GROWN BY LOW TEMPERATURE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION ON InP

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Received 29 March 1989; accepted for publication 31 March 1989

Thin films of boron nitride have been grown on InP by a low temperature (≈ 300 °C) plasma enhanced chemical vapor deposition technique. The substrates were not directly exposed to the plasma in order to minimize surface damage. The properties of the layers have been investigated by ellipsometry, X-ray photoelectron spectroscopy. $C-V_g$ characteristics on metal-insulator-semiconductor (MIS) structures have been performed. The growth rates are low, typically 30 nm/h. The layers exhibit an N/B ratio of about 0.8. The low field resistivity ranged from 10^{11} to 10^{12} Ω cm with a dielectric constant of about 5.2.

1. Introduction

InP is a promising material for high frequency and optoelectronic devices. The high electron mobility and saturation velocity, and the rather good insulator-semiconductor interfaces that have been observed, have generated considerable efforts in order to realize InP metal-insulator-semiconductor field effect transistors. Various technologies for insulator formation onto InP have been developed. However, the main impediment to use these structures in practical circuits remains the lack of stability and drift effects. It is generally believed that these effects are essentially due to phenomena occurring at the interface or in the insulator, influencing the surface potential, the effective channel mobility and giving rise to electrical instabilities related with trapping

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(North-Holland Physics Publishing Division)

levels. Therefore, more work on forming oxides and insulating films on InP is needed.

Many studies have been devoted to oxide formation and deposition of insulators like silicon dioxide, alumina or silicon nitride, whereas only little work [1,4] has been done with a material like boron nitride (BN). The stoichiometric BN is well known as being electrically insulating and chemically and thermally stable. This paper presents the results of boron nitride deposition by the plasma enhanced chemical vapor deposition (PECVD) process. This method has been largely used because it allows the deposition of films at low temperatures with properties which may be comparable to those prepared at higher temperatures by conventional CVD techniques. The procedure thus avoids excessive heating of the InP substrate whose surface is known to be thermally unstable. Further, to minimize surface damage by highly energetic particles the InP samples are placed downstream the plasma zone, corresponding to an indirect plasma enhanced CVD process.

2. Experimental details

The dielectric films were deposited using a reactor configuration shown schematically in fig. 1. The starting materials are NH_3 and an adduct which contains both nitrogen and boron like $BH_3NH(CH_3)_2$ (borane-dimethylamine (BDMA)) or $BH_3N(C_2H_5)_3$ (borane-triethylamine (BTEA)). These organic compounds were chosen as we wanted to develop a low cost and a

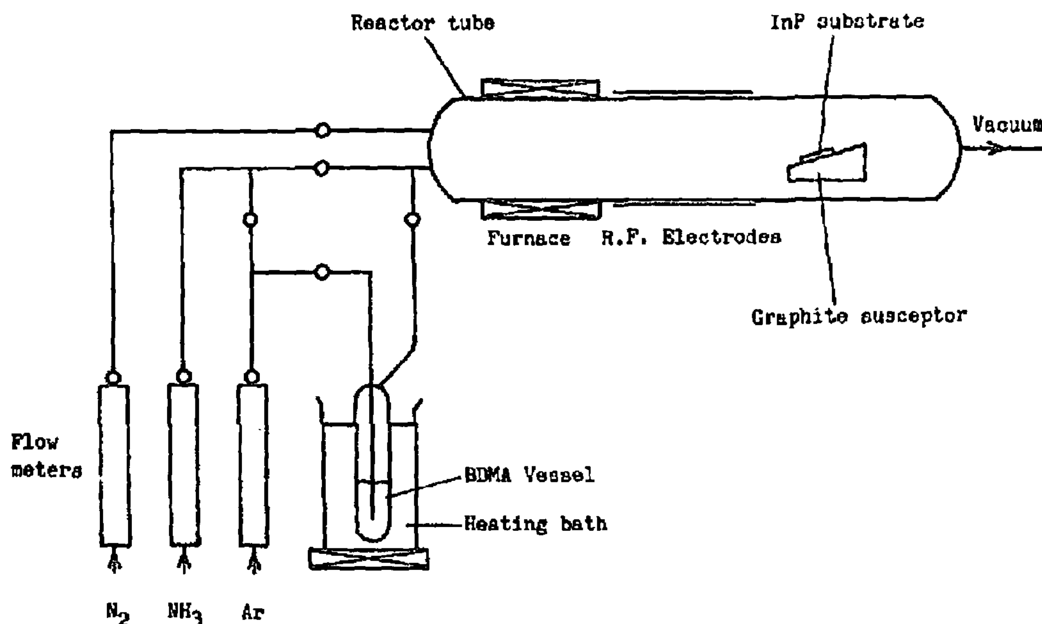

Fig. 1. Schematic diagram of the PECVD reaction system.

relatively non-toxic technique. The boron compound is heated up to 60 °C and its vapor, generated in a bubble system, is transported via a suitable carrier gas (Ar) into the reaction tube (6 cm in diameter). A pre-heating zone maintained at 430 °C is followed by the plasma zone. A maximum RF power of 50 W at 13.56 MHz was supplied through capacitive coupling between the electrodes, positioned outside the Pyrex tube. The InP samples were located downstream the plasma region, on a graphite susceptor. In this way the substrates are not directly exposed to the plasma which minimizes radiation damage to the surface. In a first experimental arrangement, the substrates were heated by an external furnace. Later, to improve the temperature control, we used a new graphite susceptor, heated itself by an electrical resistor and its temperature was maintained at 290 °C during the film deposition. The substrates used were undoped n-InP with (100) orientation supplied by Sumitomo and ICI, having a maximum carrier concentration of about 10^{16} cm^{-3}. Just prior to introduction into the reaction chamber, the samples were chemically etched in 3N HCl for 5 min, rinsed in de-ionized water and dried. The samples remained in contact with air for about 15 min before being loaded in the reactor and kept under vacuum and then in pure N_2. The chamber was repeatedly evacuated to about 10^{-2} mbar, and purged with N_2. During this interval the samples were also heated to the desired temperature. NH_3 and Ar are then introduced into the reaction zone with typical flow rates of 60 and 3 cm^3/min respectively. The pressure in the reactor was fixed between 1.5 and 1.7 mbar. A plasma power of about 50 W is then established. At the end of the deposition, the plasma power is switched off and the samples are cooled slowly under pure N_2 atmosphere.

3. Results and discussion

The thickness and the refractive index of the deposited layers were determined by ellipsometry at 632.8 nm. For these measurements the optical constants of InP were taken from the values tabulated by Aspnes and Studna [5]. With the experimental conditions described above, the growth rates are low typically 30 nm/h with BDMA and 50 nm/h with BTEA. For samples placed within the plasma zone the growth rates proved to be about 7 and 5 times greater respectively, but remained lower than the values reported by Schmolla and Hartnagel [1] who used a double-plasma process. Later the layers done with BTEA proved to be unstable in air, thus in the following, unless otherwise stated, only results concerning films obtained with BDMA are reported. The refractive index of these layers ranged from 1.60 to 1.71.

To determine the chemical composition of the films XPS studies were undertaken. Two series of samples were successively analysed. For the first set of layers the heating was achieved by an external furnace whereas for the

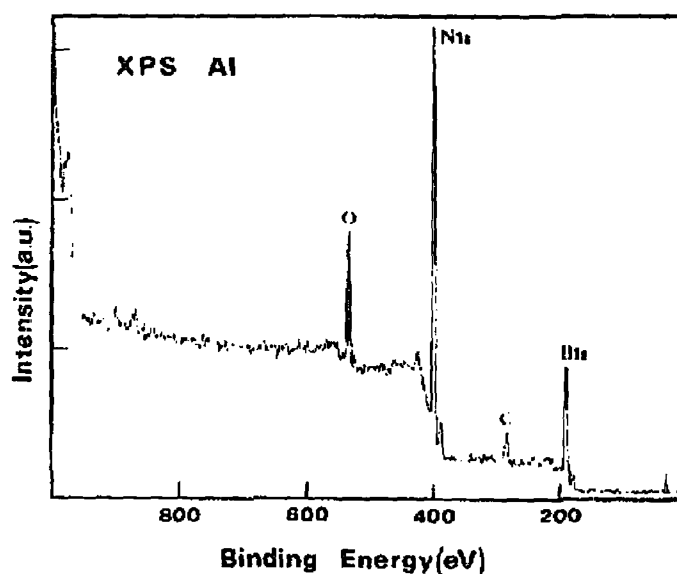

Fig. 2. XPS diagram for layers deposited with BDMA after 2 min ion etching.

second set the deposition temperature was fixed by a heated graphite susceptor as shown in fig. 1. In the first series, carbon was observed at the surface of the films, but decreased to tiny amounts after ion etching (see fig. 2). Thus nearly carbon-free films can be obtained, however in the second series a larger amount of carbon was present even after argon sputtering, and further work is needed to explain such differences. Otherwise, after ion etching, the layers exhibit nearly common trends which can be summarized as follows: oxygen remains always present with a relative O/B ratio varying around unity, the lowest values being 0.5 for some layers. This may be related to the leakage rate of the total vacuum system and to the long deposition times needed. These measurements also indicate excess boron, with a relative N/B ratio of about 0.8, showing that the active nitrogen concentration in the gas phase was not high enough. At last, the position of the peaks for B and N correspond to those given in the PHI handbook [6] for boron nitride.

For the electrical measurements metal–insulator–semiconductor (MIS) structures were prepared on samples from the second set. Ohmic contact to the back surface was achieved by thermal evaporation of Au–Ge followed by Au. Au dots were evaporated on the insulator through a metallic mask provided with circular holes of 1 mm in diameter. The capacitance–voltage characteristics were measured by the AC capacitance technique at 1 MHz while a slow bias voltage sweep was applied. Fig. 3 shows a capacitance C versus gate voltage V_g characteristic of a MIS diode with a measured insulator thickness of 43 nm (ICI substrate with a background doping of 7×10^{15} cm^{-3}). The bias sweep rate was 20 mV/s. The measurements show counterclockwise hysteresis, corresponding to ionic type instabilities, with a window width at flat band of

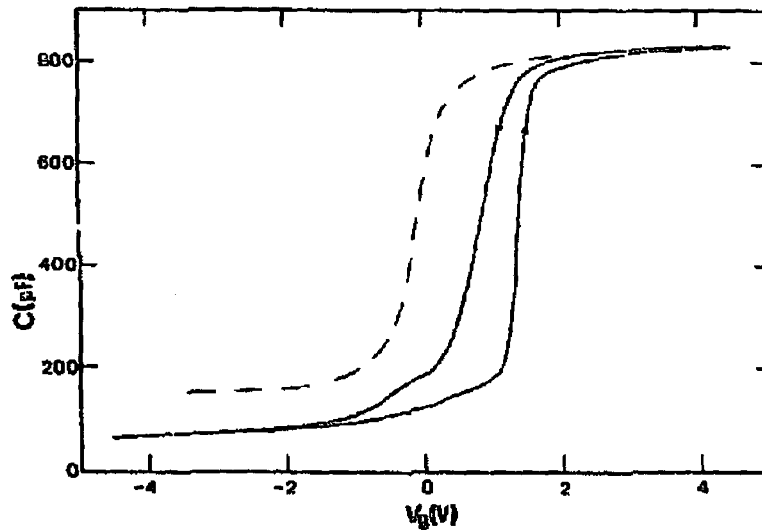

Fig. 3. Capacitance-voltage characteristic at 1 MHz of a Au/BN/InP sample. Insulating layer obtained with BDMA; thickness: 43 nm. Bias sweep rate: 20 mV/s. Dashed line, theoretical curve.

0.5 V. The flat-band voltage was estimated from the $C(V_g)$ plot using the theoretical C_{FB} value for an ideal MIS structure. The results show a large capacitance variation, and consequently a large modulation of the surface potential of the semiconductor can be obtained. The shift of the curves towards the right as compared to an ideal one corresponds to the existence of negative charges in the insulator or at the insulator–semiconductor interface. Further the experimental characteristic exhibits an irregular feature around $C \simeq 150$ pF, which may be attributed to at least a partial pinning of the Fermi level of the semiconductor. From the capacitance in accumulation and the thickness of the insulator, the dielectric constant at 1 MHz is estimated to be 5.2 ± 0.3 for most of the layers. However some less good samples showed values of about 4. The breakdown field is better than 10^6 V/cm. Metal–insulator–metal structures were prepared with gold–insulator–gold successively deposited on quartz substrates. The low field resistivities of the layers ranged from 10^{11} to 10^{12} Ωcm. These values are lower than those reported in other previous investigations for BN layers which range from 10^{14} to about 10^{16} Ωcm [2,7,8] but higher than the value obtained by Hyder and Yep [9].

4. Conclusion

We have shown the possibility of low temperature ($\simeq 300\,°$C) deposition of BN dielectric layers onto InP by a PECVD process. The layers were not free of oxygen. Direct exposure of plasma to the substrate was avoided in order to

minimize surface damage. The observed growth rates are low, and layers with small carbon content can be obtained. MIS capacitors based on these layers exhibit encouraging behavior. Nevertheless, the electrical resistivity of the insulator has to be increased. The improvement of the quality and the stability of the deposited insulator is the first step to overcome. Therefore, work is to be done to find an optimization of the process, to approach better stoichiometry and higher resistivities.

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